Chapter 3 RISK

This chapter of the Cleaner Technologies Substitutes Assessment (CTSA) addresses the health and environmental hazards, exposures, and risks that may result from using a making holes conductive (MHC) technology. The information presented here focuses entirely on MHC technologies. It does not, nor is it intended to, represent the full range of hazards or risks that could be associated with printed wiring board (PWB) manufacturing.

Section 3.1 identifies possible sources of environmental releases from MHC manufacturing and, in some cases, discusses the nature and quantity of those releases. Section 3.2 assesses occupational and general population (i.e., the public living near a PWB facility; fish in streams that receive wastewater from PWB facilities) exposures to MHC chemicals. This section quantitatively estimates inhalation and dermal exposure to workers and inhalation exposure to the public living near a PWB facility. Section 3.3 presents human health hazard and aquatic toxicity data for MHC chemicals. Section 3.4 characterizes the risks and concerns associated with the exposures estimated in Section 3.2. In all of these sections, the methodologies or models used to estimate releases, exposures, or risks are described along with the associated assumptions and uncertainties. In order to protect the identity of the proprietary chemicals, the chemical concentrations, exposures, and toxicological data for these chemicals are not given in the report. However, those proprietary chemicals that may present a potential risk to human health are identified by their generic chemical name in Section 3.4. Section 3.5 summarizes chemical safety hazards from material safety data sheets (MSDSs) for MHC chemical products and discusses process safety issues.

3.1 SOURCE RELEASE ASSESSMENT

This section of the CTSA uses data from the IPC Workplace Practices Questionnaire, together with other data sources, to identify sources and amounts of environmental releases. Both on-site releases (e.g., evaporative or fugitive emissions from the process, etc.) and off-site transfers (e.g., discharges to publicly-owned treatment works [POTWs]) are identified and, if sufficient data exist, characterized. The objectives of the Source Release Assessment are to:

- Identify potential sources of releases.
- Characterize the source conditions surrounding the releases, such as a heated bath or the presence of local ventilation.
- Where possible, characterize the nature and quantity of releases under the source conditions.

Many of these releases may be mitigated and even prevented through pollution prevention techniques and good operating procedures at some PWB facilities. However, they are included in this assessment to illustrate the range of releases that may occur from MHC processes.

A material balance approach was used to identify and characterize environmental releases associated with day-to-day operation of MHC processes. Modeling of air releases that could not be explicitly estimated from the data is done in the Exposure Assessment (See Section 3.2).

Section 3.1.1 describes the data sources and assumptions used in the Source Release Assessment. Section 3.1.2 discusses the material balance approach used and release information and data pertaining to all MHC process alternatives. Section 3.1.3 presents source and release information and data for specific MHC process alternatives. Section 3.1.4 discusses uncertainties in the Source Release Assessment.

3.1.1 Data Sources and Assumptions

This section presents a general discussion of data sources and assumptions for the Source Release Assessment. More detailed information is presented for specific inputs and releases in Sections 3.1.2 and 3.1.3.

Sources of data used in the Source Release Assessment include:

- IPC Workplace Practices Questionnaire and Performance Demonstration data (see Appendix A, Data Collection Sheets).
- Supplier-provided data, including publicly-available bath chemistry data and supplier Product Data Sheets describing how to mix and maintain baths (see Appendix B, Publicly-Available Bath Chemistry Data).
- Engineering estimates.
- The DfE PWB Project publication, *Printed Wiring Board Pollution Prevention and Control: Analysis of Survey Results* (EPA, 1995a).

Bath chemistry data were collected in the IPC Workplace Practices Questionnaire, but these data were not used due to inconsistencies in responses to the questions pertaining to bath chemistry. Instead, MHC chemical suppliers participating in the Performance Demonstration each submitted publicly-available data on their respective product lines; estimated bath concentration ranges were determined based on this information. The use of publicly-available bath chemistry data is discussed in detail in Section 2.1.4.

Several assumptions or adjustments were made to put the IPC Workplace Practices Questionnaire data in a consistent form for all MHC technologies. These include the following:

- To convert data reported on a per day basis to an annual basis, the number of days per year reported for questionnaire question 1.1 was used. For data on a weekly or monthly basis, 12 months per year and 50 weeks per year were assumed.
- If data were reported on a per shift basis, the number of shifts per day (from questionnaire question 1.4) was used to convert to a per day basis.
- Bath names in the questionnaire database were revised to be consistent with the generic MHC process descriptions in Section 2.1.3.

To facilitate comparison among process alternatives and to adjust for the wide variations in the data due to differing size of PWB facilities, questionnaire data are presented here both as

reported in the questionnaires (usually as an annual quantity consumed or produced), and normalized by annual surface square feet (ssf) of PWB produced. Normalizing the data, however, may not fully account for possible differences in processing methods that could result from higher production levels.

3.1.2 Overall Material Balance for MHC Technologies

A general material balance is presented here to identify and characterize inputs to and potential releases from the MHC process alternatives. Due to limitations and gaps in the available data, no attempt is made to perform a quantitative balance of inputs and outputs. This approach is still useful, however, as an organizing tool for discussing the various inputs to and outputs from MHC processes and presenting the available data. Figure 3.1 depicts inputs to a generalized MHC process line, along with possible outputs, including PWB product, solid waste, air emissions, and wastewater discharges. Many PWB manufacturers have an on-site wastewater treatment system for pretreating wastewaters prior to direct discharge to a stream or lake or indirect discharge to a POTW. Figure 3.2 describes a simplified PWB wastewater treatment system, including the inputs and outputs of interest in the Source Release Assessment.

Inputs

Possible inputs to an MHC process line include bath chemicals, copper-clad PWBs that have been processed through previous PWB manufacturing process steps, water, and cleaning chemicals. These inputs are described below.

- I₁ Bath chemicals used. This includes chemical formulations used for initial bath make-up, bath additions, and bath replacement. Bath formulations and the chemical constituents of those formulations were characterized based on publicly-available bath chemistry data and some proprietary bath chemistry data (see Section 2.1.4 and Appendix B). PWB manufacturers were asked to report the quantity of MHC chemicals they use annually in the IPC Workplace Practices Questionnaire, but because the resulting data were of questionable quality, total chemical usage amounts could not be quantified.
- I₂ Copper-clad PWBs. PWBs or inner layers with non-conductive drilled through-holes that come into the MHC line could add a small amount of copper to the MHC process. Trace amounts of other additives such as arsenic, chromium, and phosphate may also be introduced. This applies to all process alternatives where copper is etched off the boards in the microetch step at the beginning of the MHC process. The amount of copper added from this process is expected to be small, relative to the other chemical inputs. This would be, however, the only expected source of copper for the MHC processes where copper is not otherwise used. This input is not quantified.
- I₃ Water. Water, usually deionized, is typically used in the MHC process for rinse water, bath make-up, and equipment cleaning. The water consumption of different MHC technologies varies according to the number of rinse tanks used in the MHC process. However, the number of rinse tanks can also vary from facility to facility within a technology category due to differences in facility operating procedures and water conservation measures.

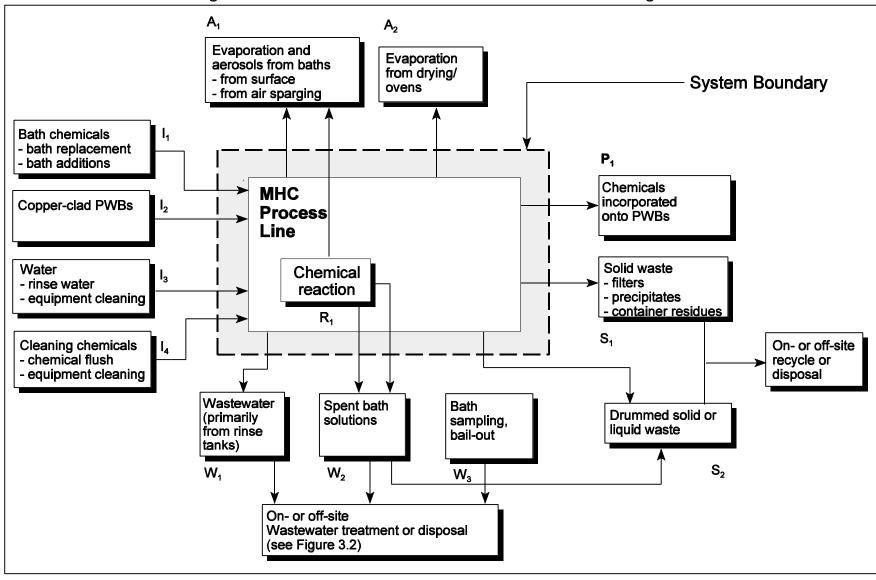


Figure 3.1 Schematic of Overall Material Balance for MHC Technologies

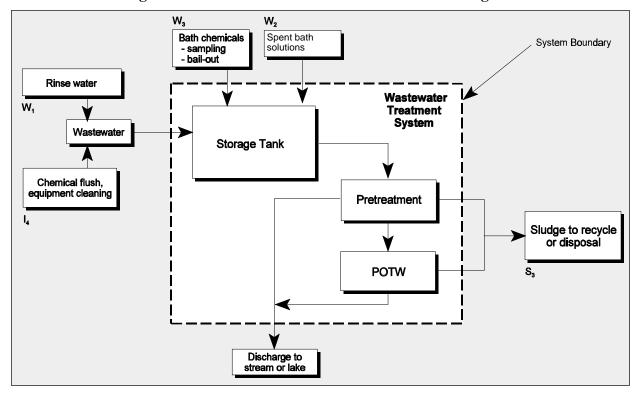


Figure 3.2 Wastewater Treatment Process Flow Diagram

Water usage data collected in the IPC Workplace Practices Questionnaire includes the annual amount of water used for bath make-up and rinse water. Annual water usage in gallons was normalized by dividing the annual water usage in gallons by annual production in ssf of PWB produced. Both annual and normalized water consumption data are summarized in Table 3.1.

Based on the normalized data, on average the questionnaire respondents with non-conveyorized MHC processes use more than ten times as much water as those with conveyorized processes. Due to the variability in questionnaire data, the relative rate of water consumption of the MHC technologies was estimated using both the questionnaire data and a simulation model of the MHC technologies. This is discussed further in Section 5.1, Resource Conservation.

I₄ Cleaning chemicals. This includes chemicals used for conveyor equipment cleaning, chemical flush, and other cleaning pertaining to the MHC process line. The amount of cleaning chemicals used is characterized qualitatively based on IPC Workplace Practices Questionnaire data and could include chemicals used to clean conveyor equipment (questionnaire question 3.5) and chemicals used in chemical flush (questionnaire question 4.4). Cleaning chemicals are discussed for specific MHC Technologies in Section 3.1.3.

The total inputs $(I_{tot}) = I_1 + I_2 + I_3 + I_4$.

Table 3.1 Water Usage of MHC Technologies

Process Type	No. of Responses	No. of Responses Water Usage (I ₃) (1,000 gal/year) ^a	
Electroless Copper			(gal/ssf) ^a
Non-conveyorized	35	180 - 16,000 (4,000)	1.2 - 120 (18)
Conveyorized	1	3,300	1
Carbon			
Conveyorized	2	330 (330)	0.28 - 0.29 (0.28)
Conductive Polymer		<u>. </u>	
Conveyorized	0	no data	no data
Graphite			
Conveyorized	4	561 - 1,200 (914)	1.2 - 3.4 (2.2)
Non-Formaldehyde E	lectroless Copper		
Non-conveyorized	1	19.5	0.36
Organic-Palladium			
Non-conveyorized	1	7,700	300
Conveyorized	1	881	1.8
Tin-Palladium			
Non-conveyorized	11	300 - 2,900 (1,600)	0.54 - 19 (7.1)
Conveyorized	2	870 - 951 (912)	0.49 - 0.68 (0.58)
All Processes			
Non-conveyorized	48	20 - 16,000 (3,400)	0.36 - 300 (21)
Conveyorized	10	330 - 3,300 (1,000)	0.28 - 3.4 (1.3)

^a Range and average values from IPC Workplace Practices Questionnaire data.

Outputs

Possible outputs from an MHC process line include PWB products with conductive hole barrels, air emissions, wastewater discharges, and solid wastes.

Product Outputs. Product outputs include:

P₁ Chemicals incorporated onto PWBs during the MHC process. This includes copper or other conductive materials deposited into the hole barrels. This output is not quantified.

Air Releases. Chemical emission rates and air concentrations are estimated by air modeling performed in the Exposure Assessment (Section 3.2). The sources of air releases and factors affecting emission rates releases are summarized below.

A₁ Evaporation and aerosol generation from baths. Potential air releases include volatilization from open surfaces of the baths as well as volatilization and aerosols generated from air sparging. These releases are quantified in the Exposure Assessment (Section 3.2). Gasses formed in chemical reactions, side reactions, and electroplating in

baths could also contribute to air releases, but these are expected to be small compared to volatilization and aerosol losses and are not quantified.

Air releases may be affected by bath temperature, bath mixing methods, and vapor control methods employed. Questionnaire data for bath agitation and vapor control methods are summarized below:¹

- Most facilities using conveyorized processes use fluid circulation to mix the baths.
 The only vapor control method reported is enclosure and venting, which is employed
 for all baths on the conveyorized lines. The process baths are completely enclosed and
 vented to the outside.
- For facilities using non-conveyorized processes, most use panel agitation and many use fluid circulation. Air sparging is used primarily in electroless copper and microetch baths. (More than one method can be used simultaneously.) Vapor control methods include push-pull for about ½ of the baths, a bath cover for about 1/4 of the baths, with enclosure and other methods reported for a few baths.²

Table 3.2 lists average bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire. Some of this information (both surface area and temperature) is used to model air releases in the Exposure Assessment. Surface areas are calculated from reported bath length and width data. Larger bath surface areas enhance evaporation. Most baths are maintained at elevated temperatures which also enhances chemical evaporation.

A₂ Evaporation from drying/oven. Air losses due to evaporation from drying steps applies primarily to carbon and graphite processes with air knife/oven steps. Releases are discussed qualitatively in Section 3.1.3.

The total outputs to air $(A_{tot}) = A_1 + A_2$.

Table 3.2 Average Bath Dimensions and Temperatures for All Processes^a

Bath	No. of Responses	Length (in.)	Width (in.)	Surface Area (sq. in.)	Volume (gal.)	Temp (°F)
Electroless Copper, non-	conveyorized					
Accelerator	31	41	23	874	123	81
Acid Dip	12	38	24	795	105	76
Anti-Tarnish	20	43	22	907	109	84
Catalyst	35	41	23	890	119	98
Conditioner/Cleaner	35	41	23	882	119	137

¹ From questionnaire question 4.1.

² Push-pull ventilation combines a lateral slot hood at one end of the tank with a jet of push air from the opposite end. It is used primarily for large surface area tanks where capture velocities are insufficient to properly exhaust fumes from the tank.

Bath	Bath No. of Length Responses (in.)		Width (in.)	Surface Area (sq. in.)	Volume (gal.)	Temp (°F)
Electroless Copper	35	45	34	1,618	229	102
Microetch	35	41	24	937	148	95
Other	9	41	16	682	116	72
Predip	35	40	23	875	117	79
Electroless Copper, cor	veyorized		1	ı	<u>I</u>	
Acid Dip	1	29	24	696	185	96
Catalyst	1	29	24	696	37	116
Conditioner/Cleaner	1	120	24	2,880	80	130
Electroless Copper	1	335	24	8,028	185	91
Microetch	1	38	24	912	54	98
Other	1	59	24	1,416	43	101
Predip	1	19	24	456	34	
Carbon, conveyorized	•		•	•	•	
Anti-Tarnish	1	23	44	1,012	25	86
Carbon	4	49	44	2,156	128	87
Cleaner	2	44	44	1,936	48	129
Conditioner	2	44	44	1,936	47	81
Microetch	2	54	44	2,354	100	116
Conductive Polymer, co	onveyorized		•		•	
Catalyst	1	48	30	1440	172	198
Conditioner/Cleaner	2	22	30	660	82	158
Microetch	1	19	30	570	82	72
Polymer	1	24	30	720	26	41
Graphite, conveyorized	l _		_	_	_	_
Anti-Tarnish	3	20	26	532	29	75
Conditioner/Cleaner	4	30	28	833	43	125
Graphite	4	30	28	833	37	82
Microetch	4	34	28	938	55	88
Non-Formaldehyde Ele	ctroless Coppe	er, non-conv	veyorized			
Accelerator	1	12	32	384	40	124
Catalyst	1	12	32	384	40	100
Conditioner/Cleaner	1	12	32	384	40	124
Electroless Copper	1	32	16	512	62	163
Microetch	1	12	32	384	40	103
Predip	1	12	32	384	40	
Organic-Palladium, no	n-conveyorized	l				
Acid Dip	1	20	63	1,260	274	70
Cleaner	1	18	63	1,134	247	122
Conditioner	1	20	63	1,260	274	105
Conductor	1	15	63	945	206	113

Bath	No. of Responses	Length (in.)	Width (in.)	Surface Area (sq. in.)	Volume (gal.)	Temp (°F)	
Microetch	1	15	63	945	206	78	
Other	1	12	63	756	157		
Post Dip	1	15	63	945	206	74	
Organic-Palladium, con	veyorized			•			
Acid Dip	1	12	49	588	24	79	
Cleaner	1	24	49	1,176	37	120	
Conditioner	1	60	49	2,940	74	100	
Conductor	1	98	49	4,802	108	115	
Microetch	1	25	49	1,225	37	75	
Other	1	24	49	1,176	48	81	
Post Dip	1	26	49	1,274	45	77	
Tin-Palladium, non-con	veyorized		•		•		
Accelerator	10	35	17	580	67	134	
Acid Dip	4	29	19	532	59	76	
Anti-Tarnish	3	34	10	344	51	73	
Catalyst	11	31	16	515	56	111	
Conditioner/Cleaner	11	34	18	576	65	164	
Microetch	9	30	17	520	64	76	
Other	4	31	18	593	61	74	
Predip	11	31	16	497	53	75	
Tin-Palladium, conveyo	rized		-		-		
Accelerator	2	40	33	1,341	80	103	
Acid Dip	2	24	33	780	53	94	
Anti-Tarnish	1	30	30	900	80	71	
Catalyst	2	86	33	2,742	173	117	
Conditioner/Cleaner	2	45	33	1,410	98	114	
Microetch	2	25	33	810	58	92	
Other	1	30	30	900	80	75	
Predip	2	24	33	780	58	81	

^a Based on IPC Workplace Practices Questionnaire data.

Water Releases. Potential outputs to water include chemical-contaminated wastewater from rinse tanks, spent bath solutions, and liquid discharges from bath sampling and bail-out. Chemical-contaminated rinse water is the largest source of wastewater from most MHC process lines and primarily results from drag-out or drag-in. Drag-out or drag-in is the transfer of chemicals from one bath to the next by dragging bath solution on a PWB out of one bath and into the subsequent bath. Drag-in or drag-out losses are estimated to be approximately 95 percent of uncontrolled bath losses (i.e., losses other than from bath replacement, bail-out, and sampling) (Bayes, 1996). The quantity of chemicals lost can be reduced through operational practices such as increased drip time (see Section 6.1, Pollution Prevention). Potential water releases are discussed further below.

- W₁ Wastewater. MHC line wastewater primarily consists of chemical-contaminated water from rinse tanks used to rinse residual chemistry off PWBs between process steps. Water usage and wastewater composition were addressed by several questions in the IPC Workplace Practices Questionnaire, with resulting data of variable to poor quality. Because the volume of rinse water used in MHC processes is much greater than water used in all other applications, the quantity of wastewater generated is assumed to be equal to water usage (I₃). The previous discussion of water usage data also applies to wastewater amounts.
- W₂ Spent bath solution. Bath concentrations vary over time (as the bath ages) and as PWBs are processed through the baths. Spent bath solutions are chemical bath solutions that have become too contaminated or depleted to properly perform a desired function. Spent bath solutions are removed from a process bath when a chemical bath is replaced.

As noted above, bath formulations and chemical constituents of those formulations were characterized based on publicly-available bath chemistry data and some proprietary bath chemistry data (see Section 2.1.4 and Appendix B). For the purposes of this assessment, chemical concentrations within the spent baths were assumed to be the same as bath make-up concentrations. The amount of spent bath disposed was addressed in the IPC Workplace Practices Questionnaire question 4.3, Chemical Bath Replacement, but many respondents did not have this information. Therefore, total chemical disposal amounts have not been quantified. Table 3.3 presents a summary of spent bath treatment methods reported in the questionnaire by MHC technology.

W₃ Bath sampling and bail-out. This includes bath solutions disposed of after sampling and analysis and bath bail-out (sometimes done prior to bath additions). In some cases sampling may be performed at the same time as bail-out if the process bath is on a controller.

Routine bail-out activities could result in a large amount of bath disposal. Because this activity was not included in the IPC Workplace Practices Questionnaire there is only limited information on frequency or amount of bail-out expected. Chemical loss due to bath sampling was assumed to be negligible.

The total outputs to water $(Wtot) = W_1 + W_2 + W_3$.

Wastewater Treatment. Figure 3.2 showed the overall water and wastewater treatment flows, including chemical bath solutions and wastewater inputs to treatment, any pre-treatment or treatment performed on-site or off-site, sludge generated from either on-site or off-site treatment, and final effluent discharge to surface water. PWB manufacturers typically combine wastewater effluent from other PWB manufacturing processes prior to on-site wastewater pretreatment. The pretreated wastewater is then discharged to a POTW.

Table 3.3 Spent Bath Treatment and Disposal Methods

Process Alternative	Total No. of Baths	Precipitation Pretreatment ^a	pH Neutralization ^a	_		Recycled On-Site ^a		Recyclea	Discharged to POTW ^a	Other Off-Site Treatment ^a
Electroless Copper, non-conveyorized	240	123	87	3	16	11	11	22	29	27
Electroless Copper, conveyorized	7	7	0	0	0	7	0	0	0	0
Carbon, conveyorized	10	7	3	0	0	0	0	0	0	0
Conductive Polymer, conveyorized	3	0	3	0	0	0	0	0	0	0
Graphite, conveyorized	13	4	8	0	2	0	1	0	4	0
Non-Formaldehyde Electroless Copper, non-conveyorized	5	0	0	0	0	0	0	0	0	0
Organic-Palladium, non-conveyorized	7	0	7	0	0	0	0	0	0	0
Organic-Palladium, conveyorized	7	4	0	0	0	0	0	0	0	0
Tin-Palladium, non-conveyorized	64	52	56	0	6	0	1	0	6	11
Tin-Palladium, conveyorized	14	4	3	0	0	0	0	0	0	0

^a Number of affirmative responses for any bath from the IPC Workplace Practices Questionnaire, for all facilities using a technology category.

Table 3.4 summarizes treatment and discharge methods and copper concentrations in PWB plant discharges reported in *Pollution Prevention and Control: Analysis of Survey Results* (EPA, 1995a). The primary purpose of most PWB manufacturer's wastewater treatment systems is the removal of dissolved metals. This is accomplished with conventional metals precipitation systems (a series of unit operations using hydroxide precipitation followed by separation of the precipitated metals), ion exchange-based metals removal systems, and combined precipitation/ion exchange systems. The most common type is conventional metals precipitation, which includes precipitation units followed by either clarifiers or membrane filters for solids separation. The use of clarifiers is the predominant method for separation of precipitated solids from the wastewater. Wastewater treatment systems are discussed further in Section 6.2, Recycle, Recovery, and Control Technologies Assessment.

Table 3.4 Treatment and Discharge Methods and Copper Concentration Summarized from Pollution Prevention and Control Survey

Respondent	Copper I	Discharge	Wastewater Wastewater	Discharge	Type of Wastewater				
Identification No.	Limit	ations	Copper		Treatment				
By MHC Technology	Max (mg/l)	Avg (mg/l)	Concentration (mg/l)						
Electroless Copper									
31838	3	1.5	NR	indirect					
36930	4.34	2.6	NR	indirect					
44486	4.5	2.7	NR	indirect	precipitation				
955703	3	2.07	0.4	indirect	electrowinning/ion exchange				
36930	2.59	1.59	1	indirect	ion exchange				
237900	2.7	1	1.2	indirect	precipitation/clarifier				
502100	1	1.5	2	indirect					
358000	2	1.5	2	indirect	ion exchange				
959951	3.22	0.45	5	indirect					
t3	2.7	2.7	5	indirect	precipitation/membrane				
44657	3	2.07	7	indirect	precipitation/clarifier				
55595	NR	NR	10	direct	precipitation/filter press				
3023	1.5	none	12.5	indirect	ion exchange, precipitation/ membrane, resist strip				
42692	4.5	2.7	17.5	direct	ion exchange				
6710	4.5	0.37	20	indirect	precipitation/clarifier				
41739	4	0.4	25	direct	precipitation/membrane				
955099	1.5	none	30	indirect	precipitation/clarifier				
t2	2.2	2.07	30	indirect	precipitation/clarifier, sludge dryer, air scrubber				
947745	3.38	2.07	30	indirect	precipitation/clarifier				
42751	3	2.07	33	indirect	precipitation/clarifier, polishing filter, filter press				

Respondent Identification No.	Limitations Copper		Discharge	Type of Wastewater Treatment	
By MHC Technology	Max (mg/l)	Avg (mg/l)	Concentration (mg/l)		
t1	1	0.03	35	direct	precipitation/clarifier, sludge dryer, chemical tester
946587	3.4	none	40	indirect	precipitation/clarifier
25503	3	2.07	40	indirect	ion exchange
965874	3.38	2.07	40	indirect	ion exchange/electrowinning
273701	3.38	2.07	50	indirect	ion exchange, electrowinning
953880	0.25	none	57	indirect	
133000	1.5	none	60	indirect	precipitation/clarifier, sludge dryer
32482	3.38	2.07	65	indirect	precipitation/clarifier
107300	2	1	80	direct	precipitation/clarifier, sludge dryer, equalization
33089	3.38	2.07	300	indirect	precip/clarifier, filter press
3470	1.5	2.07		indirect	ion exchange
Graphite					
43841	4.3	2.6	200	indirect	precipitation/filtration, filter press, equalization, etc.
Palladium					
279	3	2.02	NR	direct	
37817 ^a	4.5	3.5	3	indirect	ion exchange, electrowinning
29710	0.49	0.41	4	direct	ion exchange
43694	3	2.07	30	indirect	ion exchange
Average	2.75	1.50	35.70		
Median	3	2.07	30		
Max	4.50	3.50	300.00		
Min	0.25	0.03	0.2		
Standard Deviation	1.20	0.97	57.54		as with Endard records in a

^a Respondent 37817 reported Cu max = 5.0 mg/l; assumed 4.5 mg/l in compliance with Federal regulations.

NR: Not Reported. Source: EPA, 1995a.

Following any in-house wastewater treatment, facilities release wastewater either directly to surface water or indirectly to a POTW. Sludge from on-site wastewater treatment is discussed in the section below (Solid Waste). The data for discharge type (direct or indirect) are discussed for specific processes in Section 3.1.3.

Permit data for releases were not collected; this was deleted from the questionnaire upon request by industry participants. However, PWB manufacturers who responded to the IPC

Workplace Practices Questionnaire were asked to provide the maximum and average metals concentrations (e.g., copper, palladium, tin) in wastewater from their MHC line (questionnaire question 2.3, Wastewater Characterization). Several respondents indicated the question could not be answered, did not respond to this question, or listed their POTW permit discharge limits. This is because there are many sources of metals, especially copper, in PWB manufacturing. PWB manufacturers typically combine effluents from different process steps prior to wastewater treatment. Thus, the chemical constituents and concentration in wastewater could not be characterized.

Solid Waste. Solid wastes are generated by day-to-day MHC line operation and by wastewater treatment of MHC line effluents. Some of these solid wastes are recycled, while others are sent to incineration or land disposal. Solid waste outputs include:

- Solid waste. Solid wastes could include spent bath filters, chemical precipitates (e.g., CuSO₄ crystals from etch bath), packaging or chemical container residues, and other solid waste from the process line, such as off-specification PWBs. Chemical baths are typically replaced before precipitation occurs. However, if precipitation does occur, some precipitates, such as copper sulfate crystals, may be recycled. Container residue is estimated by EPA to be up to four percent of the chemicals use volume (Froiman, 1996). An industry reviewer indicated this estimate would only occur with very poor housekeeping practices and is not representative of the PWB industry (Di Margo, 1996). The questionnaire data did not include chemical characterization of solid wastes.
- S₂ Drummed solid or liquid waste. This includes other liquid or solid wastes that are drummed for on-site or off-site recycling or disposal. Some spent baths and wastes can be recycled or recharged, such as etchant. No data were available to characterize these wastes.
- S₃ Sludge from on-site wastewater treatment. Questionnaire respondents were asked to report the amount of sludge they generated during on-site wastewater treatment that could be attributed to MHC line effluents (questionnaire question 2.4, Wastewater Discharge and Sludge Data). Both annual quantities and data normalized to pounds of sludge per ssf of PWB produced are presented in Table 3.5. However, many PWB manufacturers have indicated that the amount of sludge from the MHC process cannot be reliably estimated since effluents from various PWB manufacturing process steps are combined prior to wastewater treatment. In addition, the amount of sludge generated during wastewater treatment varies according to the MHC technology used, the treatment method used, facility operating procedures, the efficiency with which bath chemicals and rinse water are used, and other factors. Thus, the comparative amount of sludge generated due to the choice of an MHC technology could not be determined, nor were data available to characterize the concentrations of metals contributed by the MHC line.

The total solid waste output $(S_{tot}) = S_1 + S_2 + S_3$.

Table 3.5 Sludge Generation from Wastewater Treatment of MHC Line Effluents

Process Type	No. of Responses	Sludge (S ₄) (lbs/year) ^a	Sludge (S_4) $(lbs/1,000 ssf)^a$	
Electroless Copper				
Non-conveyorized	35	600 - 100,000 (25,000)	2 - 530 (96)	
Conveyorized	1	1,000	0.31	
Carbon				
Conveyorized	2	no data	no data	
Conductive Polyme	er	<u>.</u>		
Conveyorized	0	no data	no data	
Graphite		<u>.</u>		
Conveyorized	4	5.5 - 920 (380)	0.01 - 5.6 (2.2)	
Non-Formaldehyde	e Electroless Copper	•		
Non-conveyorized	1	200	3.7	
Organic-Palladium	1			
Non-conveyorized	1	5,000	190	
Conveyorized	1	21,600	45	
Tin-Palladium				
Non-conveyorized	11	200 - 24,000 (6,700)	1.3 - 94 (27)	
Conveyorized	2	17,000	9.5	
All Processes		_		
Non-conveyorized	48	200 - 100,000 19,500)	1.3 - 530 (79)	
Conveyorized	10	5.5 - 21,600 (6,800)	0.01 - 45 (10)	

^a Range and average values for each from questionnaire data.

Transformations. Transformations within the MHC system boundary could include:

R₁ Chemical reaction gains or losses. This includes any chemical species consumed, transformed, or produced in chemical reactions and side reactions occurring in the process baths. Reactions and side reactions within the baths could result in either chemical losses or production of new chemicals as degradation products. One important set of reactions involve formaldehyde in the electroless copper process. Formaldehyde, which is utilized as a reducing agent, is converted to formic acid. In a secondary or side reaction formaldehyde also breaks down into methanol and the formate ion. This reaction is the only source of formate ion in the electroless copper bath. Other side reaction products include BCME (bis-chloromethyl ether) which is produced in a reaction between hydrochloric acid and formaldehyde (Di Margo, 1996).

The overall material balance: $I_{tot} = A_{tot} + W_{tot} + S_{tot} + P_1 \pm R_1$.

3.1.3 Source and Release Information For Specific MHC Technology Categories

This section describes the specific inputs and outputs in the material balance for each MHC technology. To facilitate comparison among process alternatives, and to adjust for the wide variations in the data due to differing sizes of PWB facilities, data are presented both as reported in the IPC Workplace Practices Questionnaire, and normalized by production amounts (annual ssf of PWB produced). Average values from the IPC Workplace Practices Questionnaire database are reported here for summary purposes.

Electroless Copper Process

Figure 3.3 illustrates the generic electroless copper process steps and typical bath sequence evaluated in the CTSA. The process baths depicted in Figure 3.3 represent an integration of the various products offered within the electroless copper technology category. The number and location of rinse steps shown in the figure are based on the IPC Workplace Practices Questionnaire data. Figure 3.3 lists the types and sequence of baths in a generic electroless copper line, but the types and sequence of baths in an actual line could vary.

Water Usage (I_3) and Wastewater (W_1). Water usage data from the IPC Workplace Practices Questionnaire were presented in Table 3.1; the amount of wastewater generated is assumed equal to the amount of water used. Of respondents using an electroless copper process, 11 discharge wastewater directly to a stream or river following the appropriate treatment while 20 facilities use indirect discharge (e.g., to a POTW). (Five facilities did not respond to the question.) While several facilities using electroless copper completed the questionnaire, only a single facility used the conveyorized process. This large facility produces over three million ssf of PWB per year. In summary:

- Reported water usage for the facility using a conveyorized electroless copper process is 3.3 million gallons per year, or about one gallon per ssf of PWB produced.
- Reported water usage for the facilities using non-conveyorized processes average 4.0 million gallons per year, or 18 gallons per ssf of PWB produced.

Chemical constituents and concentrations in wastewater could not be adequately characterized.

Cleaning Chemicals (I_4). Chemicals used for cleaning of electroless copper equipment, as reported in the IPC Workplace Practices Questionnaire, include water, sodium persulfate, sulfuric acid, hydrogen peroxide, nitric acid, and "211 solvent."

Bath Chemicals Used (I₁). Appendix B presents estimated bath chemical concentrations for the electroless copper process. The amount of bath chemicals used could not be quantified from questionnaire data.

Spent Bath Solutions (W₂). The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods were presented in Table 3.3. Precipitation pretreatment and on-site recycling are reported treatment methods for the conveyorized electroless copper process; precipitation pretreatment and pH neutralization were most commonly reported as methods for the non-conveyorized electroless copper process.

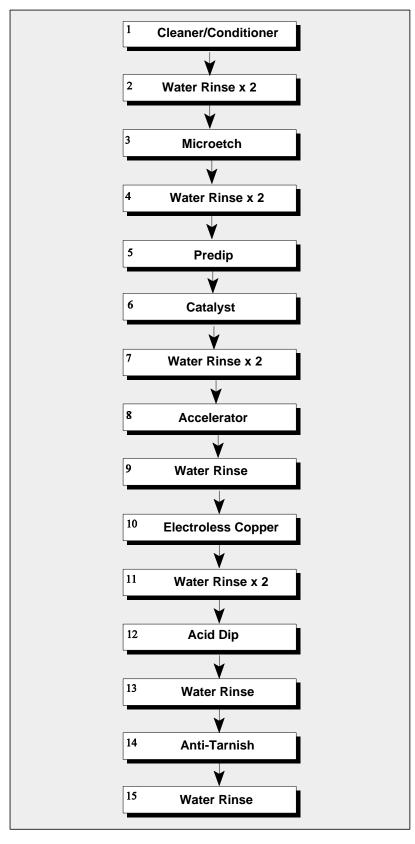


Figure 3.3 Generic Electroless Copper Process Steps and Typical Bath Sequence

Evaporation From Baths (A_1). Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize questionnaire data:

- For the single conveyorized electroless copper process, fluid circulation is used in all but the microetch bath. Enclosure is used for vapor control for all baths.
- For non-conveyorized electroless copper facilities, panel agitation is used in most baths, fluid circulation in about 1/3 of the baths, air sparging is primarily used in electroless copper and a few microetch baths, and a few baths use other mixing methods. Vapor control methods include push-pull for about ½ of the baths, a bath cover for about 1/4 of the baths, with enclosure and other methods reported for a few of the baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire.

Evaporation From Drying/Oven (A_2) . This source of air emissions does not apply to electroless copper processes since oven drying is not required and air drying immediately follows water rinsing.

Chemicals Incorporated Onto PWBs (P_1). Copper is added to the boards in the electroless copper process. Small quantities of palladium from the catalyst are also deposited on the PWBs.

Drummed Solid or Liquid Waste (S_2). This was reported as a spent bath treatment method for either solution or sludge for 16 out of 240 baths by the non-conveyorized electroless copper facilities (see Table 3.3). The total quantity of drummed waste was not reported.

Sludge Amounts From On-Site Treatment (S_3) . Sludge generation data are presented in Table 3.5. In general:

- Reported sludge amounts for the facility using a conveyorized process are 1,000 lbs/year, or 0.31 lbs per 1,000 ssf of PWB produced.
- Reported sludge amounts for the facilities using non-conveyorized processes average 25,000 lbs/year, or 96 lbs per 1,000 ssf of PWB produced.

Metal concentrations in sludge could not be adequately characterized.

Chemical Reaction Gains or Losses (R_1). The most well-documented chemical reactions in electroless copper baths involve formaldehyde. Formaldehyde is used as a copper reducing agent, and in this reaction formaldehyde is converted to formic acid and hydrogen gas. In a secondary (unwanted) reaction called the Cannizzaro reaction, formaldehyde breaks down to methanol and the formate ion which in a caustic solution forms sodium formate. A study by Merix Corporation found that for every one mole of formaldehyde reacting in the intended copper deposition process, approximately one mole was reacting with hydroxide in the Cannizzaro reaction. Other studies have found that the side reaction tendency goes up with the alkalinity of the process bath (Williamson, 1996). A search of literature references failed to produce sufficient quantifiable data to characterize these reactions.

Carbon Process

Figure 3.4 illustrates the carbon process steps and bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.4 lists the types and sequence of baths in a generic carbon line, but the types and sequence of baths in an actual line could vary. Both carbon facilities in the IPC Workplace Practices Questionnaire database use conveyorized equipment.

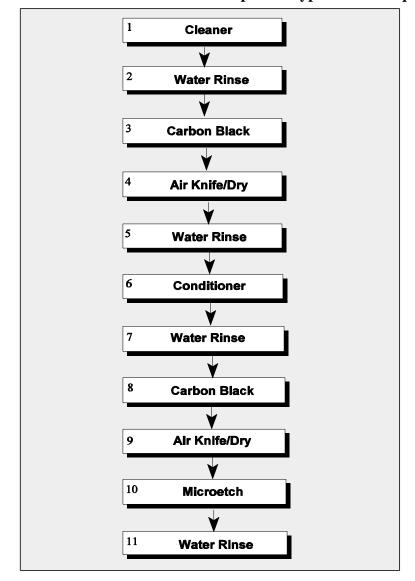


Figure 3.4 Generic Carbon Process Steps and Typical Bath Sequence

Water Usage (I₃) and Wastewater (W₁). Water usage data were summarized in Table 3.1; wastewater generation is assumed equal to water usage. Reported water usage for the two facilities is 330,000 gallons per year, or 0.28 gallon per ssf of PWB produced. Both carbon facilities use indirect discharge of wastewater. Chemical constituents and concentrations in wastewater could not be adequately characterized.

Cleaning Chemicals (I_4). Only water is used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire.

Bath Chemicals Used (I₁). Appendix B presents estimated bath chemical concentrations for the carbon process. The amount of bath chemicals used could not be quantified from the data.

Spent Bath Solutions (W₂). The quantity of spent bath solution could not be determined from available data. Spent bath treatment methods were presented in Table 3.3. Precipitation pretreatment and pH neutralization are reported methods for carbon processes.

Evaporation From Baths (A_1). Air releases are modeled in the Exposure Assessment (Section 3.2). For both facilities using conveyorized carbon, fluid circulation is used for bath agitation and enclosure is used for vapor control for all baths. Table 3.2 lists bath surface area, volume, and bath temperature data.

Evaporation From Drying/Oven (A₂). Air knife/oven drying occurs after the carbon black and fixer steps. Any solution adhering to the boards would be either blown off the boards and returned to the sump, or volatilized in the oven. Air emissions from air knife/oven drying were not modeled.

Chemicals Incorporated Onto PWBs (P_1) . Carbon black is added to the boards in this process.

Drummed Solid or Liquid Waste (S_2). This was not reported as a spent bath treatment method for carbon processes (see Table 3.3).

Sludge Amounts From On-Site Treatment (S_3) . Sludge data were not reported for the carbon processes.

Conductive Ink Process

A generic conductive ink sequence is shown in Figure 3.5. Source release data for conductive ink are not available since there are no facilities currently using the process for the production of multi-layer PWBs.

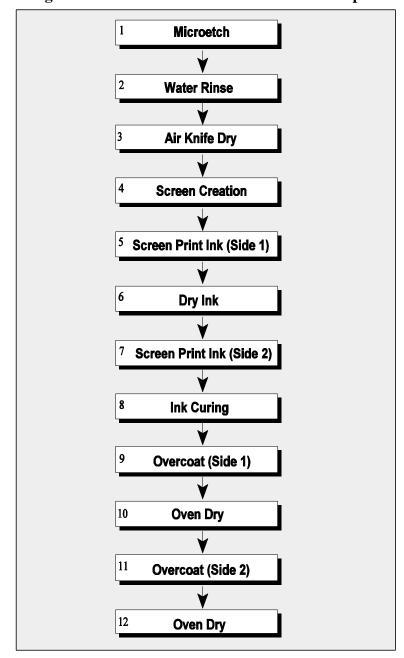


Figure 3.5 Generic Conductive Ink Process Steps

Conductive Polymer Process

Figure 3.6 illustrates the generic conductive polymer process steps and typical bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.6 lists the types and sequence of baths in a generic conductive polymer line, but the types and sequence of baths in an actual line could vary. The single conductive polymer facility in the IPC Workplace Practices Questionnaire data uses conveyorized equipment.

Water Usage (I_3) and Wastewater (W_1) . The single facility using a conductive polymer process uses indirect discharge of wastewater.

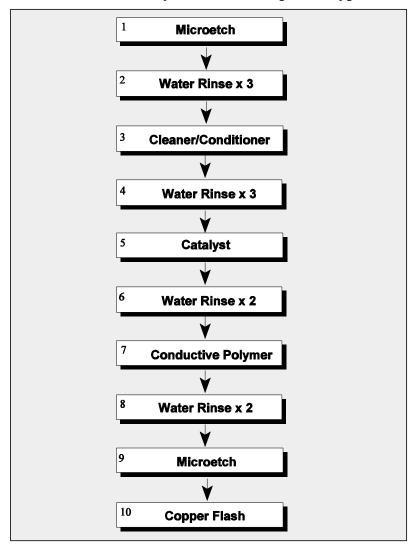


Figure 3.6 Generic Conductive Polymer Process Steps and Typical Bath Sequence

Cleaning Chemicals (I_4). Only water is used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire data.

Bath Chemicals Used (I₁). Appendix B presents estimated bath chemical concentrations for the conductive polymer process. The amount of bath chemicals used could not be quantified from the data.

Spent Bath Solutions (W₂). The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods are presented in Table 3.3. pH neutralization is reported as a treatment method for the conductive polymer process.

Evaporation From Baths (A_1). Air releases are modeled in the Exposure Assessment (Section 3.2). The facility using a conveyorized conductive polymer process reported using fluid circulation for all baths and enclosure for vapor control for all baths. Table 3.2 shows bath surface area, volume, and bath temperature data.

Evaporation From Drying/Oven (A_2). This source of air emissions does not apply to the conductive polymer process since oven drying is not required and air drying immediately follows water rinsing.

Chemicals Incorporated Onto PWBs (P_1) . A polymer is added to the boards in this process.

Drummed Solid or Liquid Waste (S_2). This was not reported as a spent bath treatment method for the conductive polymer process (see Table 3.3).

Sludge Amounts From On-Site Treatment (S_3). Sludge amounts were not reported for this process.

Graphite Process

Figure 3.7 illustrates the generic graphite process steps and typical bath sequence evaluated in the CTSA. The process baths depicted in Figure 3.7 represent an integration of the various products offered within the graphite technology category. The number and location of rinse steps shown in the figure are based on the IPC Workplace Practices Questionnaire data. Thus, Figure 3.7 lists the types and sequence of baths in a generic graphite line, but the types and sequence of baths in an actual line could vary. The four facilities in the IPC Workplace Practices Questionnaire database use conveyorized equipment.

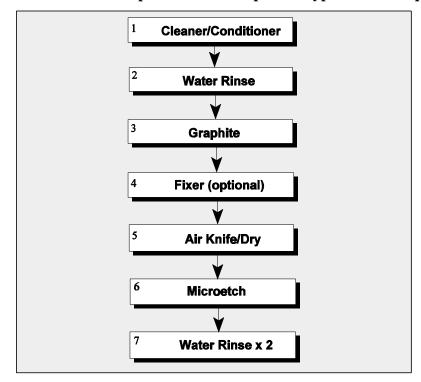


Figure 3.7 Generic Graphite Process Steps and Typical Bath Sequence

Water Usage (I_3) and Wastewater (W_1). Water usage data are presented in Table 3.1. For graphite, two facilities use direct and two facilities use indirect discharge. Reported water usage for the facilities using a conveyorized process averages 914,000 gallons per year, or 2.2 gallons per ssf of PWB produced.

Cleaning Chemicals (I₄). Chemicals used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire, include water and ammonia.

Bath Chemicals Used (I₁). Appendix B presents estimated bath chemical concentrations for the graphite process. The amount of chemicals used could not be determined from the data.

Spent Bath Solutions (W₂). Spent bath treatment methods are presented in Table 3.3. Precipitation pretreatment, pH neutralization, and discharge to a POTW are reported methods for the graphite process.

Evaporation From Baths (A_1). Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize Workplace Practices data:

- For facilities using a conveyorized graphite process, fluid circulation is used in most baths. Enclosure for vapor control is employed for all of the baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire.

Evaporation From Drying/Oven (A₂). Air knife/oven drying occurs after the graphite and fixer steps. Any solution adhering to the boards would be either blown off the boards and returned to the sump, or volatilized in the oven. Air emissions from air knife/oven drying were not modeled.

Chemicals Incorporated Onto PWBs (P_1) . Graphite is added to the boards in this process.

Drummed Solid or Liquid Waste (S_2). This was reported as a spent bath treatment method for two out of 13 baths by the facilities using a conveyorized graphite process (see Table 3.3).

Sludge Amounts From On-Site Treatment (S_3). Sludge generation data are presented in Table 3.5. Reported sludge amounts for the facilities using a conveyorized process average 380 lbs/year, or 2.2 lbs per 1,000 ssf of PWB produced.

Non-Formaldehyde Electroless Copper Process

Figure 3.8 illustrates the generic non-formaldehyde electroless copper process steps and typical bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.8 lists the types and sequence of baths in a generic non-formaldehyde electroless copper line, but the types and sequence of baths in an actual line could vary. The single non-formaldehyde electroless

copper facility in the IPC Workplace Practices Questionnaire database uses a non-conveyorized equipment configuration. This is a small facility that produces just over 50,000 ssf of PWB per year.

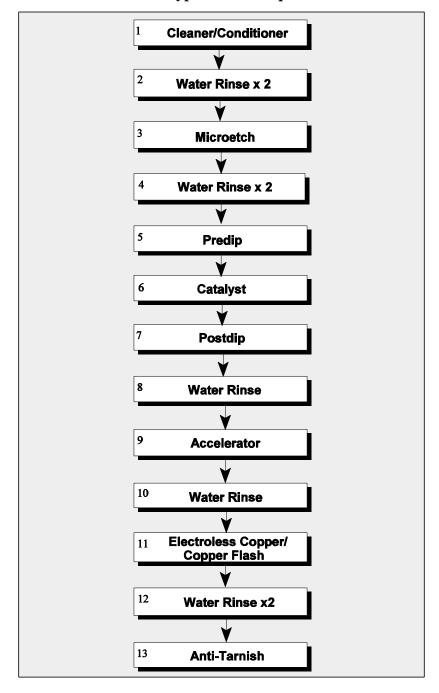


Figure 3.8 Generic Non-Formaldehyde Electroless Copper Process Steps and Typical Bath Sequence

Water Usage (I_3) and Wastewater (W_1) . Water usage data for the single non-formaldehyde electroless copper facility in the IPC Workplace Practices Questionnaire database were presented in Table 3.1; wastewater generation is assumed equal to water usage. The non-formaldehyde electroless copper facility indicated it discharges wastewater directly to a receiving

stream, rather than a POTW. Chemical constituents and concentrations in wastewater could not be adequately characterized.

Cleaning Chemicals (I_4). Only water is used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire.

Bath Chemicals Used (I₁). Appendix B presents estimated bath chemical concentrations for the non-formaldehyde electroless copper process. The amount of bath chemicals used could not be quantified from data.

Spent Bath Solutions (W₂). The quantity of spent bath solutions could not be determined from available data. Spent bath treatment methods are presented in Table 3.3. No treatment methods were reported for the non-formaldehyde electroless copper process.

Evaporation From Baths (A_1). Air releases are modeled in the Exposure Assessment (Section 3.2). The non-formaldehyde electroless copper facility uses panel agitation in all baths and fluid circulation in most baths. The only vapor control method reported is the use of a removable bath cover for the microetch bath. Table 3.2 lists bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire.

Evaporation From Drying/Oven (A₂). This source of air emissions does not apply to non-formaldehyde electroless copper processes since oven drying is not required and air drying immediately follows water rinsing.

Chemicals Incorporated Onto PWBs (P_1) . Copper is added to the boards in the non-formaldehyde electroless copper process.

Drummed Solid or Liquid Waste (S_2). This was not reported as a spent bath treatment method for the non-formaldehyde copper facility (see Table 3.3).

Sludge Amounts From On-Site Treatment (S₃). These data are presented in Table 3.5. Reported sludge amounts for the non-formaldehyde electroless copper facility are 200 lbs/year, or 3.7 lbs per 1,000 ssf of PWB produced. Metal concentrations in sludge were not characterized.

Organic-Palladium Process

Figure 3.9 illustrates the generic organic-palladium process steps and bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.9 lists the types and sequence of baths in a generic organic-palladium line, but the types and sequence of baths in an actual line could vary. One organic-palladium facility in the IPC Workplace Practices Questionnaire database uses conveyorized equipment; the other uses non-conveyorized equipment.

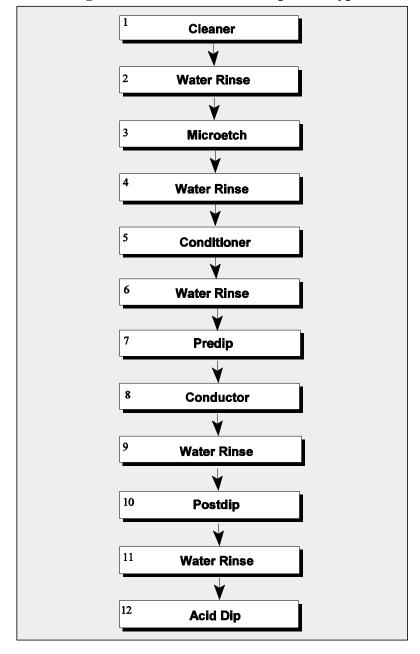


Figure 3.9 Generic Organic-Palladium Process Steps and Typical Bath Sequence

Water Usage (I_3) and Wastewater (W_1) . Water usage data from the questionnaire were presented in Table 3.1; wastewater generation is assumed equal to water usage. Of the two respondents using organic-palladium, one discharges directly to a stream or river following the appropriate treatment and one discharges to a POTW. In summary:

- Reported water usage for the facility using a conveyorized process is 881,000 gallons per year, or 1.8 gallons per ssf of PWB produced.
- Reported water usage for the facility using a non-conveyorized process is 7.7 million gallons per year, or 300 gallons per ssf of PWB produced.

Cleaning Chemicals (I₄). Chemicals used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire, include water, nitric acid, hydrogen peroxide, sulfuric acid, and iron chloride.

Bath Chemicals Used (I₁). Appendix B presents estimated bath chemical concentrations for the organic-palladium process. The amount of bath chemicals used could not be quantified from the data.

Spent Bath Solutions (W₂). The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods are presented in Table 3.3. Precipitation pretreatment was reported for conveyorized organic-palladium and pH neutralization for non-conveyorized organic-palladium processes.

Evaporation From Baths (A_1). Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize the data:

- For the organic-palladium facility using a conveyorized process, fluid circulation is reported for most of the baths and enclosure is used for vapor control for all baths.
- For the organic-palladium facility using a non-conveyorized process, panel agitation and fluid circulation are reported for most baths. Push-pull is used as a vapor control method for most baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data.

Evaporation From Drying/Oven (A_2). This source of air emissions does not apply to the organic-palladium process since oven drying is not required and air drying immediately follows water rinsing.

Chemicals Incorporated Onto PWBs (P_1) . Palladium is added to the board in this process.

Drummed Solid or Liquid Waste (S_2). This was not reported as a spent bath treatment method for organic-palladium processes (see Table 3.3).

Sludge Amounts From On-Site Treatment (S_3). These data are presented in Table 3.5. In summary:

- Reported sludge amounts for the facility using a conveyorized process were 21,600 lbs/year, or 45 lbs per 1,000 ssf of PWB produced.
- Reported sludge amounts for the facility using a non-conveyorized process were 5,000 lbs/year, or 190 lbs per 1,000 ssf of PWB produced.

Metal concentrations in sludge could not be adequately characterized.

Tin-Palladium Process

Figure 3.10 illustrates the generic tin-palladium process steps and bath sequence evaluated in the CTSA. The process baths depicted in Figure 3.10 represent an integration of the various products offered within the tin-palladium technology category. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.10 lists the types and sequence of baths in a generic tin-palladium line, but the types and sequence of baths in an actual line could vary. Thirteen tin-palladium facilities are in the IPC Workplace Practices Questionnaire database. Of these, two use conveyorized equipment and 11 use non-conveyorized.

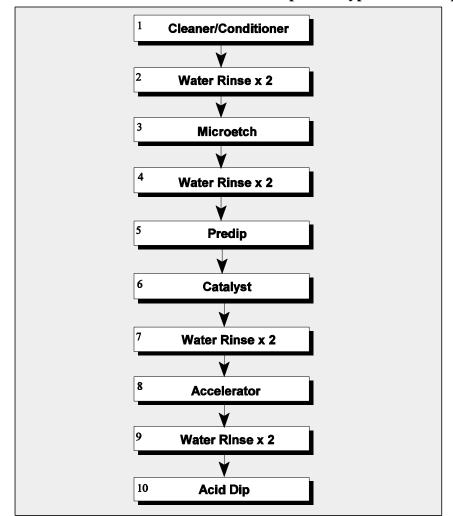


Figure 3.10 Generic Tin-Palladium Process Steps and Typical Bath Sequence

Water Usage (I_3) and Wastewater (W_1). Water usage data from the IPC Workplace Practices Questionnaire were presented in Table 3.1; wastewater generation is assumed equal to water usage. Of respondents using tin-palladium, two discharge wastewater directly to a stream or river following the appropriate treatment while ten facilities use indirect discharge (e.g., to a POTW). (One facility did not respond to the question.) In summary:

- Reported water usage for the facilities using conveyorized processes average 912,000 gallons per year, or 0.58 gallons per ssf of PWB produced.
- Reported water usage for the facilities using non-conveyorized processes average 1.6 million gallons per year, or 7.1 gallons per ssf of PWB produced.

Cleaning Chemicals (I₄). Chemicals used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire, include water, sodium hydroxide, hydrochloric acid, and nitric acid.

Bath Chemicals Used (I₁). Appendix B presents estimated bath chemical concentrations for the tin-palladium process. The amount of bath chemicals used could not be quantified from the data.

Spent Bath Solutions (W₂). The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods are presented in Table 3.3. Precipitation pretreatment and pH neutralization are the only reported methods for the conveyorized process and are the most commonly reported methods for the non-conveyorized tin-palladium process.

Evaporation From Baths (A_1). Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize questionnaire data:

- For the conveyorized tin-palladium process, fluid circulation is reported as a mixing method for all of the baths and enclosure is used for vapor control for all baths.
- For the non-conveyorized tin-palladium processes, panel agitation is used in about 2/3 of the baths, fluid circulation in about ½ of the baths, and air sparging for 1/3 of the microetch baths. Vapor control methods include push-pull and enclosure for a few baths, and covering for about 1/3 of the baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data.

Evaporation From Drying/Oven (A_2). This source of air emissions does not apply to tin-palladium processes since oven drying is not required and air drying immediately follows water rinsing.

Chemicals Incorporated Onto PWBs (P_1) . Palladium and small quantities of tin are added to the board in the tin-palladium process.

Drummed Solid or Liquid Waste (S_2). This was reported as a spent bath treatment method for six out of 64 baths by the facilities with non-conveyorized tin-palladium processes (see Table 3.3). The total quantity of drummed waste was not reported.

Sludge Amounts From On-Site Treatment (S₃). Sludge data are presented in Table 3.5. In general:

• Reported sludge amounts for the conveyorized facilities average 17,000 lbs/year, or 9.5 lbs per 1,000 ssf of PWB produced.

• Reported sludge amounts for the non-conveyorized facilities average 6,700 lbs/year, or 27 lbs per 1,000 ssf of PWB produced.

Metal concentrations in sludge could not be adequately characterized.

3.1.4 Uncertainties in the Source Release Assessment

Uncertainties and variations in the data include both gaps in knowledge (uncertainty) and variability among facilities and process alternatives. These are discussed below.

For the IPC Workplace Practices Questionnaire and Performance Demonstration data:

- There may be uncertainties due to misinterpretation of a question, not answering a question that applies to that facility, or reporting inaccurate information. Also, because of a limited number of responses for the alternative processes, information more typical for that process may not be reported.
- Variation includes variation within or among process alternatives, or difference due to PWB ssf produced. Again, for MHC process alternatives with a limited number of responses, statistical summaries of the data may be precluded, and data may not be representative of most PWB facilities.

For the supplier-provided data:

- Knowledge gaps include a lack of information on proprietary chemicals, incomplete bath composition data, and the reporting of wide ranges of chemical concentrations on a MSDS rather then specific amounts in the formulations.
- Variation includes variation in bath chemistries and process specifications among suppliers for a given process alternative. The publicly-available bath chemistry data, chemical concentrations, and supplier recommendations may not apply to a specific facility due to variation in process set-up and operation procedures.

Other uncertainties pertain to the applicability and accuracy of estimates and assumptions used in this assessment.

3.2 EXPOSURE ASSESSMENT

Evaluating exposure for the PWB CTSA involves a series of sequential steps. The first step is characterizing the exposure setting, which includes describing the physical setting and characterizing the population(s) of interest and their activities that may result in exposure. These are described in Section 3.2.1 for both workplace and surrounding population (ambient) exposure.

The next step is selecting a set of workplace and population exposure pathways for quantitative evaluation from the set of possible exposure pathways. This is discussed in Section 3.2.2.

Next, chemical concentrations are collected or estimated in all media where exposure could occur. For the MHC processes, this consists of collecting existing concentration data from workplace monitoring, estimating the chemical concentrations in the MHC baths, and performing fate and transport modeling to estimate workplace and ambient air concentrations (Section 3.2.3).

The exposure-point concentrations and other exposure parameters are combined in exposure models to estimate potential dose rates (PDRs) for all quantified pathways. These exposure models and parameter values are described in Section 3.2.4. The final step, characterizing uncertainties, is in Section 3.2.5.

Because this CTSA is a comparative evaluation, and standardization is necessary to compare results for the alternative processes, this assessment focuses on a "model" (generic) PWB facility and uses aggregated data. In addition, this assessment focuses on exposure from chronic, long-term, day-to-day releases from a PWB facility rather than short-term exposures to high levels of hazardous chemicals as there could be with a fire, spill, or periodic releases. Due to the limited resources available to the project and the lack of information to characterize such releases, high level, acute exposures could not be assessed.

3.2.1 Exposure Setting

Characterizing the exposure setting includes the following steps:

- Characterizing the physical environment (in this case, a model PWB facility, its MHC process area, and the surrounding environment).
- Identifying potentially exposed workers and their activities.
- Identifying any potentially exposed populations, human or ecological, that may be exposed through releases to the ambient environment from PWB facilities.
- Defining the exposure scenarios to evaluate. (As used here, the term *scenario* refers to a specified physical setting, exposed population, and activities that may result in exposure.)

Physical Environment

IPC Workplace Practices Questionnaire and Performance Demonstration data collected for 59 PWB facilities and their MHC process areas were used to characterize a model PWB facility. Information obtained from these sources includes the following:

- Regarding MHC process alternatives, the IPC Workplace Practices Questionnaire database includes information from 36 electroless copper facilities, two carbon facilities, one conductive polymer facility, four graphite facilities, one non-formaldehyde copper facility, two organic-palladium facilities, and 13 tin-palladium facilities.
- Of these facilities, 48 are independent and the other 11 are original equipment manufacturers (OEMs) who manufacture PWBs solely for use in that company's products.
- The size of the PWB manufacturing area ranges from 3,721 to 400,000 ft², with a geometric mean area of 33,800 ft².
- The size of the MHC process room ranges from 120 to 60,000 ft², with a geometric mean of 3,760 ft².
- The number of days per year the MHC line operates ranges from 80 to 360, with an average of 250 days/year and a 90th percentile of 306 days/year.
- The total PWB processed per year ranges from 24,000 ssf per year to 6.24 million ssf per year, with a geometric mean of 351,670 ssf per year.
- Temperature of the process room ranges from 60 to 94 °F, with an average of 75 °F.
- All 59 facilities responding to the question reported the use of some type of ventilation in the process area. A smaller number of facilities provided more specific information on the type of ventilation and air flow rates. Reported air flow rates range from 7 to 405,000 ft³/min. with a geometric mean of 6,100 ft³/min. Of the facilities reporting air flow rates, the types of ventilation reported are as follows:
 - Seven facilities reported using both local and general ventilation systems.
 - Six facilities reported using only general ventilation.
 - Twenty-three facilities reported using only local ventilation. (However, they may not have consistently reported general ventilation.)
 - One facility did not specify either local or general ventilation.

The initial intent was to focus on a generic small- to medium-sized facility that manufactures $\leq 6{,}000$ ssf of PWB per day. However, larger facilities are now included in the database to account for all of the performance demonstration sites and all categories of process alternatives. The conductive ink facility is not included in this assessment.

The data summarized here are used to broadly characterize the exposure setting (i.e., a model PWB facility and MHC process area). Data used in the exposure models are discussed further in Section 3.2.4. Based on the workplace practices data and using arithmetic averages or geometric means, a model facility has the following characteristics:

- Is independent (rather than OEM).
- Uses 33,800 ft² of facility space in the PWB operation.
- Contains the MHC process in a room 3,760 ft² in size.
- Operates an MHC line 250 days/year.
- Manufactures 350,000 ssf of PWB per year.
- Is 75 °F in the process room.
- Has a typical ventilation air flow rate in the process area of 6,100 ft³/min.

Potentially Exposed Populations

Potentially exposed populations include both workers in the PWB facilities and ecological and human populations in the vicinity of the facilities. Each of these populations is discussed briefly below.

General Employee Information from the IPC Workplace Practices Questionnaire.

A summary of IPC Workplace Practices Questionnaire data pertaining to employees at PWB facilities includes the following:

- The number of full-time employee equivalents (FTEs) ranges from 8 to 1,700, with a geometric mean of 103.
- The number of employee work days per year ranges from 200 to 360, with an average of 268 days/year. The number of days per year the MHC line operates is used to characterize worker exposure from MHC line operation, rather than the overall employee work days per year, because the latter could include workers not in the MHC process area or time when the MHC line is not in operation.
- The MHC process line operates from 1 to 12 hours/shift, with an average of 6.8 hours/shift.
- Fifty-eight out of 59 facilities reported a first shift, 52 a second shift, 29 a third shift, and one reported a fourth shift (one facility operates the second but not a first shift). For MHC operation, 54 facilities reported a first shift, 43 a second shift, 16 a third shift, and one reported a fourth shift. This exposure assessment uses first shift data as representative.
- Types of workers in the MHC process area include:
 - Line operators.
 - Laboratory technicians.
 - Maintenance workers.
 - Supervisory personnel.
 - Wastewater treatment operators.
 - Contract workers.
 - Other employees (i.e., manufacturing engineer, process control specialist).

General Population Outside the Facility. PWB facilities included in the IPC Workplace Practices Questionnaire and Performance Demonstration database are located in various cities in the U.S. and Europe. Many are in southern California. This assessment estimates potential exposure to a hypothetical community living near a model PWB facility.

Exposure to ecological populations could also occur outside a PWB facility. In past CTSAs, concentrations have been estimated for surface water to assess potential exposure to aquatic organisms. However, as discussed in the Source Release Assessment (Section 3.1), data limitations preclude estimating releases to surface water. Ecological toxicity and hazard for potential releases to surface water (based on bath constituents used in each alternative) are addressed in Section 3.3.

Workplace Exposure Scenarios

A scenario describes the exposure setting, potentially exposed populations or individuals, and activities that could lead to exposure. For workplace exposures, the setting involves the MHC process in a PWB facility. The Workplace Practices data are used here to determine the types of workers who may be exposed and to characterize those worker's activities. Worker activities include working in the process area, MHC line operation, chemical bath sampling, chemical bath additions, chemical bath replacement, rack cleaning, conveyor equipment cleaning, and filter replacement.

Working in the Process Area. Exposure via inhalation of airborne chemicals is possible to workers in the MHC process area. Because of this, the questionnaire included questions about the types of workers who might be present in the area. Out of 59 facilities responding to this question:

- Fifty-nine have line operators in the MHC process area during the first shift.
- Fifty-two have laboratory technicians in the MHC process area.
- Thirty-eight have maintenance workers in the MHC process area.
- Fifty have supervisory personnel in the MHC process area.
- Thirty-six have wastewater treatment operators in the MHC process area.
- Two have contract workers in the MHC process area.
- Six have other employees in the MHC process area.

MHC Line Operation. Potential for exposure during MHC line operation is expected to vary significantly among process methods. In manual, non-conveyorized methods, a line operator stands at the bath and manually lowers and raises the panel racks into and out of each bath. A vertical/automated method is completely automated, where panel racks are lowered and raised into vertical tanks by a robotic arm; line operators load and unload panels from the racks. A manually-controlled vertical hoist is a semi-automated system where racks are lowered into and raised out of a series of vertical chemical baths by a line operator-controlled hoist. The hoist is controlled by a hand-held control panel attached to the hoist by a cable. The conveyorized method is an automated method where panels are transported into and out of process baths by means of a conveyor; line operators load and unload panels from the conveyor system. Based on the workplace practices data:

- For electroless copper lines, 35 out of 36 are non-conveyorized, of which 19 are vertical/automated, ten are manually controlled vertical hoist, and six are manual (with no automation). One facility is conveyorized.
- All carbon and graphite lines in the database are conveyorized.
- The single conductive polymer system is conveyorized.
- The single non-formaldehyde electroless copper system is non-conveyorized, with manually controlled vertical hoist.
- For organic-palladium lines, one is conveyorized and one is non-conveyorized with a vertical/automated system.
- For tin-palladium lines, 13 are non-conveyorized, of which one is vertical/automated, four are manually controlled vertical hoist, and six are manual (no automation). Two facilities are conveyorized.

Different assumptions are made about worker exposure for non-conveyorized and conveyorized systems. For the non-conveyorized systems, it is assumed that workers manually lower and raise panel racks. This is a conservative but consistent assumption made for all non-conveyorized process alternatives.

Chemical Bath Sampling. Based on the questionnaire database, chemical baths in the carbon, graphite, and organic-palladium alternatives are normally sampled by use of a drain or spigot on the bath. For electroless copper, the most common method is to dip a container (ladle, beaker, or sample bottle) into a bath. For tin-palladium, the most common method reported is to sample by pipette.

Chemical Bath Additions. Methods of chemical additions from the database are as follows:

- Most facilities pour chemical additions directly into the bath or tank (63 percent).
- Other reported options include: stirring into a tank (24 percent), pouring into an automated chemical addition system (20 percent), or other (two percent). Stirring typically involves fluid agitation while pouring the formulation into the bath.
- For carbon and graphite facilities, 100 percent reported pouring directly into the tanks.

This activity is characterized for a model facility by pouring chemicals directly into the tank for all process alternatives except conductive polymer, where all additions are made automatically.

Chemical Bath Replacement. This process includes removing the spent bath, cleaning the empty tank, and making up fresh bath solutions. In this process, a worker could be exposed to chemicals in the spent bath, on the inside walls of the emptied bath, or to chemicals in the new bath solution.

Rack Cleaning. Rack cleaning only applies to those process alternatives where a buildup of material on the panel racks occurs (e.g., copper plating onto the racks). This includes the electroless copper, non-formaldehyde electroless copper, and tin-palladium processes. Rack cleaning for these processes could occur either as part of the routine MHC line operation (called "continuous" rack cleaning) or as a separate step in the process. Of the facilities responding to this question, only nine out of 36 electroless copper facilities and four out of 13 tin-palladium facilities reported rack cleaning as a separate step in the process. An additional 17 electroless copper facilities reported continuous rack cleaning. All of the remaining facilities reported the question was not applicable, did not respond, or gave an unusable response.

Because there were a low number of applicable or usable responses to the question, and a majority of the electroless copper facilities responding to the question use continuous rack cleaning, this activity is not considered quantitatively as a separate worker activity performed at a model facility.

Conveyor Equipment Cleaning. Conveyor equipment cleaning involves regular equipment maintenance for conveyorized MHC lines; 11 of the facilities in the database are conveyorized. Examples include cleaning the fluid circulation heads and rollers for the graphite process, and vacuuming particulates from the drying areas of graphite and carbon lines.

Filter Replacement. Filter replacement could result in exposure to the material on the filter or in the bath. Whether the pathway is significant to worker risk will depend, in part, on the chemical constituents in the bath.

Use of Personal Protective Equipment (PPE). An overview of the data pertaining to the use of PPE indicates the following general trends for the various activities:

- Most facilities reported the use of eye protection and gloves, but some did not.
- Use of lab coats or aprons was reported approximately 1/4 to $\frac{1}{2}$ of the time.
- Few facilities reported using boots.
- The use of respiratory protection was very rarely reported.

It is assumed that the only PPE used is eye protection and that the line operator's hands and arms may contact bath solutions. This is a conservative but consistent assumption for all process alternatives and worker activities, particularly for dermal exposure. While most PWB facilities reported that line operators do wear gloves, the assumption that the line operator's hands and arms may contact bath solutions is intended to account for the fraction of workers who do not. For workers who do wear gloves, dermal contact exposure is expected to be negligible.

Summary of Scenarios. *MHC Line Operators*. In general, line operators perform several activities, including MHC line operation (which includes working in the MHC process area); chemical bath replacement; rack cleaning; conveyor equipment cleaning; filter replacement; chemical bath sampling; making chemical bath additions; and bail-out of baths. Some kind of local ventilation is typically used for the process line.

There are two different scenarios for line operators depending on process configuration. For non-conveyorized processes, dermal exposure could occur through routine line operation as well as bath maintenance activities. Inhalation exposure could occur throughout the time period a line operator is in the MHC process area. Conveyorized processes are enclosed and the line operator does not contact the bath solutions in routine line operation; he or she only loads panels at the beginning of the process and unloads them at the end of the process. For conveyorized processes, dermal exposure is primarily expected through bath maintenance activities such as bath replacement, bath sampling, and conveyor equipment cleaning. Because the conveyorized lines are enclosed and typically vented to the outside, inhalation exposure to line operators and other workers is assumed to be negligible for the conveyorized processes.

Laboratory Technicians. In general, laboratory technicians perform one activity pertaining to the MHC line, chemical bath sampling, in addition to working in the MHC process area. Bath sampling exposure is quantified separately for laboratory technicians.

Other Workers in the MHC Process Area. Other workers in the MHC process area may include maintenance workers, supervisory personnel, wastewater treatment operators, contract workers, and other employees. They perform activities not directly related to the MHC line, but typically spend some time in the MHC process area. Because the line operators spend the most amount of time per shift, exposure via inhalation is quantified for them (for non-conveyorized processes), and characterized for the other employees in terms of the time spent in the process area relative to line operators.

3.2.2 Selection of Exposure Pathways

The definition of exposure scenarios leads to selection of the exposure pathways to be evaluated. An exposure scenario may comprise one or several pathways. A complete exposure pathway consists of the following elements:

- A source of chemical and mechanism for release.
- An exposure point.
- A transport medium (if the exposure point differs from the source).
- An exposure route.

Tables 3.6 and 3.7 present an overview of the pathways selection for workplace and surrounding population exposures, respectively. For the workplace, another potential pathway not quantified is oral exposure to vapors or aerosols. For example, oral exposure could occur if inhaled chemicals are coughed up and then swallowed.

Population exposures may occur through releases to environmental media (i.e., releases to air, water, and land). The only pathway for which exposure is estimated is inhalation of chemicals released from a facility to a nearby residential area. Approaches for the three environmental media are described below.

Air

Air releases from the MHC process are modeled for the workplace. Those modeled emission rates are used in combination with an air dispersion model to estimate air concentrations to a nearby population.

Surface Water

Little reliable data are available for water releases for the MHC alternatives. (This issue is discussed further in Section 3.2.3.) Exposures and risks from surface water are evaluated qualitatively by identifying chemicals potentially released to surface water from the publicly-available bath chemistry data (discussed in Section 2.1.4), bath chemistry data for disclosed proprietary ingredients, and using ecological toxicity data to highlight those chemicals of highest ecological concern if released to surface water (Section 3.3).

Land

Possible sources of releases to land from MHC processes include bath filters and other solid wastes from the process line, chemical precipitates from baths, and sludge from wastewater treatment. These are discussed in Section 3.1, Source Release Assessment. Reliable characterization data for potential releases to land are not available; therefore, the exposure assessment does not estimate the nature and quantity of leachate from landfills or effects on groundwater.

 Table 3.6 Workplace Activities and Associated Potential Exposure Pathways

Activities	Potential Pathways	Evaluation Approach and Rationale
Line Operators ^a	· ·	**
MHC Line Operation	Dermal contact with chemicals in MHC baths.	Exposure quantified for non-conveyorized lines; the highest potential dermal exposure is expected from this activity. Exposure for conveyorized lines assumed to be negligible for this activity.
	Inhalation of vapors or aerosols from MHC baths.	Exposure quantified for non-conveyorized lines. Exposure for conveyorized lines assumed to be negligible.
Working in Process Area	Inhalation of vapors or aerosols from MHC baths.	Exposure quantified for non-conveyorized lines.
Chemical Bath Replacement; Conveyor Equipment Cleaning; Filter Replacement; Chemical Bath Sampling	Dermal contact with replacement chemicals.	Exposure quantified for conveyorized lines for all activities together (bath sampling quantified separately for laboratory technicians). Exposure not quantified separately for these activities on non-conveyorized lines.
	Inhalation of vapors or aerosols from MHC baths.	Not quantified separately. Included in "working in process area" for non-conveyorized lines; not quantified due to modeling limitations for conveyorized lines.
Rack Cleaning	Dermal contact with chemicals on racks.	Not quantified; limited data indicate this is not performed by many facilities.
	Inhalation of vapors or aerosols from MHC baths.	Not quantified separately. Included in "working in process area" for non-conveyorized lines; not quantified due to modeling limitations for conveyorized lines.
Chemical Bath Additions	Dermal contact with chemicals added.	Not quantified separately from chemicals already in the baths.
	Inhalation of vapors or aerosols from MHC baths or while making bath additions.	Not quantified separately. Included in "working in process area" for non-conveyorized lines; not quantified due to modeling limitations for conveyorized lines.
Laboratory Technicians		
Chemical Bath Sampling	Dermal contact with chemicals in MHC baths.	Exposure quantified for conveyorized and non-conveyorized lines.
	Inhalation of vapors or aerosols from MHC baths.	Not quantified separately (included in "working in process area").
Working in Process Area	Inhalation of vapors or aerosols from MHC baths.	Exposure quantified for line operators for non-conveyorized lines; exposure for other workers is proportional to their exposure durations.

Activities	Potential Pathways	Evaluation Approach and Rationale			
Maintenance Workers, Supervisory Personnel, Wastewater Treatment Operators, Contract Workers, and Other Workers					
Working in Process Area	Inhalation of vapors or aerosols from MHC baths.	Exposure quantified for line operators for non-conveyorized lines; exposure for other workers is proportional to their exposure durations.			
	Dermal contact with chemicals in MHC baths.	Not quantified. ^a			

^a This assumes MHC line operators are the most exposed individuals and perform all direct maintenance on the MHC line, including filter replacement and equipment cleaning.

Table 3.7 Potential Population Exposure Pathways

Population	Potential Pathways	Evaluation Approach and Rationale
Residents Living Near a PWB	Inhalation of chemicals released to air.	Exposure quantified for all potential carcinogens and any other chemical released at a rate of at least 23 kg/year.
Facility	Contact with chemicals released to surface water directly or through the food chain.	Not evaluated.
	Exposure to chemicals released to land or groundwater.	Not evaluated.
Ecological	Exposure to chemicals released to surface water.	Evaluated qualitatively in the Human Health and Ecological Hazards Summary (Section 3.3).
	Exposure to chemicals released to air or land.	Not evaluated.

3.2.3 Exposure-Point Concentrations

The term exposure-point concentration refers to a chemical concentration in its transport or carrier medium, at the point of contact (or potential point of contact) with a human or environmental receptor. Sources of data for the Exposure Assessment include monitoring data, publicly-available bath chemistry data, some proprietary bath chemistry data, and fate and transport models to estimate air releases and air concentrations. Concentrations for dermal exposure in the baths are those estimated from publicly-available bath chemistry data, as described in Section 2.1.4, and from disclosed proprietary ingredient information. Fate and transport modeling were performed to estimate air concentrations for workplace and surrounding population exposures as described in this section.

Monitoring Data

Table 3.8 presents a summary of all available Federal Occupational Safety and Health Administration (OSHA) data for PWB manufacturers (standard industrial code [SIC] 3672). California OSHA was also consulted for monitoring data; they referred to the Federal OSHA database. In addition, one facility submitted results of monitoring for formaldehyde at 0.06 ppm (8 hr. time-weighed average [TWA]) along with their response to the IPC Workplace Practices Questionnaire.

It should be noted that OSHA monitoring is typically performed only for those chemicals which are regulated by OSHA (i.e., chemicals with permissible exposure limits [PELs]). Monitoring also does not distinguish between the MHC process and other parts of the PWB process that may be located in the same area.

Table 3.8 Summary of Federal OSHA Monitoring Data for PWB Manufacturers (SIC 3672)

(515 50.2)						
No. of Data Points/ No. of Facilities	Range (ppm)	Average (ppm) ^a	Standard Deviation (ppm)			
26 / 6	0 - 27	6.9	8.24			
11 / 2	0 - 0	0	0			
5 / 1	0 - 0.09	0.02	0.04			
43 / 11	0 - 4.65	0.44	0.75			
26 / 5	0 - 0	0	0			
16 / 4	0 - 215	41.7	57.6			
6 / 1	0 - 0	0	0			
3 / 1	0 - 0	0	0			
33 / 6	0 - 2.3	0.359	0.614			
26 / 10	0 - 0.113	0.006	0.023			
28 / 11	0 - 0.24	0.045	0.070			
	No. of Facilities 26 / 6 11 / 2 5 / 1 43 / 11 26 / 5 16 / 4 6 / 1 3 / 1 33 / 6 26 / 10	No. of Facilities (ppm) 26 / 6 0 - 27 11 / 2 0 - 0 5 / 1 0 - 0.09 43 / 11 0 - 4.65 26 / 5 0 - 0 16 / 4 0 - 215 6 / 1 0 - 0 3 / 1 0 - 0 33 / 6 0 - 2.3 26 / 10 0 - 0.113	No. of Facilities (ppm) (ppm) ^a 26 / 6 0 - 27 6.9 11 / 2 0 - 0 0 5 / 1 0 - 0.09 0.02 43 / 11 0 - 4.65 0.44 26 / 5 0 - 0 0 16 / 4 0 - 215 41.7 6 / 1 0 - 0 0 3 / 1 0 - 0 0 33 / 6 0 - 2.3 0.359 26 / 10 0 - 0.113 0.006			

^a Zeros were included in averages; detection limits were not reported.

Modeling Workplace Air Concentrations

Bath concentrations estimated from publicly-available chemistry data and disclosed proprietary chemical data, as well as process configurations from the IPC Workplace Practices Questionnaire, were used to estimate workplace and ambient air concentrations using fate and transport models (Robinson et al., 1997). This section describes air transport models to estimate worker inhalation exposure to chemicals from PWB MHC lines. Three air transport models are used to estimate worker exposure:

- 1. Volatilization of chemicals induced by air sparging.
- 2. Aerosol generation induced by air sparging.
- 3. Volatilization of chemicals from the open surface of MHC tanks.

For models 1 and 3, volatilization was modeled only for those chemicals with a vapor pressure above 10⁻³ torr (a vapor pressure less than 10⁻³ torr was assumed for inorganic salts even if vapor pressure data were not available). Aerosol generation and volatilization from air-sparged baths were modeled only for those baths that are mixed by air sparging as indicated in the Workplace Practices and Performance Demonstration data; this includes the electroless copper baths and some cleaning tanks. The total transport of chemicals from the air-sparged baths was determined by summing the releases from each of the three models. The third model was applied to determine volatilization of chemicals from un-sparged baths. A review of the relevant literature, descriptions of the models, and examples demonstrating the use of the models are available in the December 22, 1995 Technical Memorandum, *Modeling Worker Inhalation*

Exposure (Appendix D). Modeled emission rates and workplace air concentrations are presented in Table 3.9. Proprietary chemical results are not presented in order to protect proprietary chemical identities.

Table 3.9 Results of Workplace Air Modeling

Table 3.9 Results of Workplace Air Modeling						
Chemical ^a	Emission Rate (mg/min)	Air Conc. (mg/m³)	Federal OSHA and/or NIOSH Permissible Inhalation Exposure Limits (mg/m³) ^b			
Electroless Copper, non-conveyorized		_				
Ammonium Chloride	NA	NA	10 (NIOSH)			
Benzotriazole	1.24e-01	5.54e-03				
Boric Acid	1.71e-01	7.64e-03				
Copper (I) Chloride	7.56e-02	3.38e-03	1 (as Cu dust and mist; OSHA/NIOSH)			
Copper Sulfate; or Cupric Sulfate	8.31e-02	3.71e-03	1 (as Cu dust and mist; OSHA/NIOSH)			
Dimethylaminoborane	1.94e+00	8.66e-02				
Dimethylformamide	1.42e+00	6.33e-02	30 (OSHA/NIOSH)			
2-Ethoxyethanol	1.46e+03	6.51e+01	740 (OSHA); 1.8 (NIOSH)			
Ethanolamine	9.92e+00	4.44e-01	6 (OSHA)			
Ethylene Glycol	3.33e+00	1.49e-01				
Ethylenediaminetetraacetic Acid (EDTA)	5.11e-01	2.29e+02				
Fluoroboric Acid	2.20e+00	9.82e-02				
Formaldehyde	1.37e+01	6.15e-01	0.94 (0.75 ppm) ^c (OSHA)			
Formic Acid	3.51e+01	1.57e+00	9 (OSHA/NIOSH)			
Hydrochloric Acid	5.43e-03	2.43e-04	7 (NIOSH)			
Hydrogen Peroxide	1.66e-01	7.41e-03	1.4 (OSHA/NIOSH)			
Hydroxyacetic Acid	3.14e-02	1.40e-03				
Isopropyl Alcohol; or 2-Propanol	5.24e+02	2.34e+01	980 (OSHA)			
m-Nitrobenzene Sulfonic Acid	9.14e-04	4.09e-05				
Magnesium Carbonate	9.99e-03	4.47e-04				
Methanol	2.31e+02	1.03e+01	260 (OSHA/NIOSH)			
p-Toluene Sulfonic Acid	NA	NA				
Palladium	NA	NA				
Peroxymonsulfuric Acid	2.15e-01	9.60e-03				
Potassium Bisulfate	1.15e-01	5.14e-03				
Potassium Cyanide	2.52e-03	1.13e-04	5 (as CN; OSHA/NIOSH)			
Potassium Hydroxide	2.33e-03	1.04e-04	2 (NIOSH)			
Potassium Persulfate	8.16e-02	3.65e-03				
Potassium Sulfate	1.60e-01	7.15e-03				
Potassium-Sodium Tartrate	3.55e-01	1.59e-02				
Sodium Bisulfate	NA	NA				
Sodium Carbonate	5.65e-04	2.53e-05				

Chemical ^a	Emission Rate (mg/min)	Air Conc. (mg/m³)	Federal OSHA and/or NIOSH Permissible Inhalation Exposure Limits (mg/m³) ^b
Sodium Chlorite	NA	NA	
Sodium Cyanide	2.61e-03	1.17e-04	5 (as CN; OSHA/NIOSH)
Sodium Hydroxide	1.18e-01	5.26e-03	2 (OSHA/NIOSH)
Sodium Hypophosphite	NA	NA	
Sodium Sulfate	NA	NA	
Stannous Chloride	NA	NA	2 (as Sn; OSHA)
Sulfuric Acid	1.24e+00	5.57e-02	1 (OSHA)
Tartaric Acid	1.17e-02	5.21e-04	
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	NA	NA	
Non-Formaldehyde Electroless Copper	, non-conve	yorized	
Copper Sulfate; or Cupric Sulfate	2.74e-01	1.22e-02	1 (as Cu dust and mist; OSHA/NIOSH)
Hydrochloric Acid	NA	NA	7 (NIOSH)
Hydrogen Peroxide	9.36e-02	4.19e-03	1.4 (OSHA/NIOSH)
Isopropyl Alcohol; or 2-Propanol	7.34e+01	3.28e+00	980 (OSHA)
Potassium Hydroxide	1.49e-03	6.67e-05	2 (NIOSH)
Potassium Persulfate	5.68e-02	2.54e-03	
Sodium Chlorite	NA	NA	
Sodium Hydroxide	1.74e-03	7.78e-05	2 (OSHA/NIOSH)
Stannous Chloride	NA	NA	2 (as Sn; OSHA)
Sulfuric Acid	1.48e-01	6.63e-03	1 (OSHA)
Organic-Palladium, non-conveyorized			
Hydrochloric Acid	NA	NA	7 (NIOSH)
Sodium Bisulfate	NA	NA	
Sodium Carbonate	NA	NA	
Sodium Hypophosphite	NA	NA	
Sodium Persulfate	NA	NA	
Trisodium Citrate 5.5-Hydrate; or Sodium Citrate	NA	NA	
Tin-Palladium, non-conveyorized			
1,3-Benzenediol	NA	NA	
Copper (I) Chloride	NA	NA	1 (as Cu dust and mist; OSHA/NIOSH)
Copper Sulfate; or Cupric Sulfate	7.38e-02	3.30e-03	1 (as Cu dust and mist; OSHA/NIOSH)
Ethanolamine	2.00e+01	8.92e-01	6 (OSHA)
Fluoroboric Acid	1.76e+00	7.89e-02	
Hydrochloric Acid	NA	NA	7 (NIOSH)
Hydrogen Peroxide	9.71e-02	4.34e-03	1.4 (OSHA/NIOSH)
Isopropyl Alcohol; or 2-Propanol	2.94e+02	1.32e+01	980 (OSHA)

Chemical ^a	Emission Rate (mg/min)	Air Conc. (mg/m³)	Federal OSHA and/or NIOSH Permissible Inhalation Exposure Limits (mg/m³) ^b
Lithium Hydroxide	NA	NA	
Palladium	NA	NA	
Palladium Chloride	NA	NA	
Potassium Carbonate	NA	NA	
Sodium Bisulfate	NA	NA	
Sodium Chloride	NA	NA	
Sodium Hydroxide	NA	NA	2 (OSHA/NIOSH)
Sodium Persulfate	8.38e-01	3.75e-02	
Stannous Chloride	NA	NA	2 (as Sn; OSHA)
Sulfuric Acid	1.16e-01	5.19e-03	1 (OSHA)
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	NA	NA	
Vanillin	8.09e-02	3.62e-03	

^a Proprietary chemical results are not presented in order to protect proprietary chemical identities.

NA: Not Applicable. A number was not calculated because the chemical's vapor pressure is below the 1×10^{-3} torr cutoff and is not used in any air-sparged bath. Therefore, air concentrations are expected to be negligible.

Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the " \times 10" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as 1.2 \times 10⁴, which is the same as 0.00012 in common decimal notation.

Volatilization of Chemicals from Air-Sparged MHC Tanks. Mixing in plating tanks (e.g., the electroless copper plating tank) is commonly accomplished by sparging the tank with air. The equation used for predicting the mass transfer rate from an aerated system is based on volatilization models used in research of aeration in wastewater treatment plants:

$$F_{y,s} = Q_G H_y c_{L,y} \left[1 - \exp \left(-\frac{K_{OL,y} a V_L}{H_y Q_G} \right) \right]$$

where:

 $F_{v.s}$ = mass transfer rate of chemical y out of the system by sparging (mg/min)

 O_G = gas flow rate (L/min)

 H_v = dimensionless Henry's Law Constant (H_c) for chemical y

 $c_{I,v}$ = concentration of chemical y in bulk liquid (mg/L)

K_{OL,y} = overall mass transfer coefficient for chemical y (cm/min) a = interfacial area of bubble per unit volume of liquid (cm²/cm³)

 V_{I} = volume of liquid (cm³)

Aerosol Generation from Baths Mixed by Sparging with Air. Aerosols or mists are also a potential source of contaminants from electroless baths. The rate of aerosol generation has been found to depend on the air sparging rate, bath temperature, air flow rate above the bath, and

^b Source: NIOSH, 1994 and 29 CFR 1910.1000, Table Z-1.

^c OSHA has set an "action level" of 0.5 ppm for formaldehyde. At or above that level, people working in the area of exposure must be monitored, and the area must be segregated. From 0.1 - 0.5 ppm, workers must be notified that formaldehyde is present (but not that it is suspected of being a carcinogen).

the distance between bath surface and the tank rim. The following equation is used to estimate the rate of aerosol generation (Berglund and Lindh, 1987):

$$R_A = [5.5x10^{-5}(Q_G / A) + 0.01] F_T F_A F_D$$

where:

 R_A = aerosol generation rate (ml/min/m²)

 Q_G = air sparging rate (cm³/min)

A = bath area (m^2)

 F_T = temperature correction factor F_A = air velocity correction factor

 F_D = distance between the bath surface and tank rim correction factor.

The emission of contaminants resulting from aerosols depends on both the rate of aerosol generation and the concentration of contaminants in the aerosol. The following equation is used to estimate contaminant emission (flux) from aerosol generation:

$$F_{y,a} = \frac{M_I}{M_b} f_{IE} F_{y,s}$$

where:

 F_{va} = rate of mass transfer from the tank to the atmosphere by aerosols (mg/min)

 f_{IE} = fraction of bubble interface ejected as aerosols (dimensionless)

M_I = mass of contaminant at the interface (mg) M_b = mass of contaminant in gas bubble (mg)

The literature on aerosol generation indicates that the typical size of aerosols is one to ten microns; this is important to note because particles in this range are more inhalable. Larger sized particles tend to fall back into baths rather than remaining airborne and dispersing throughout the room.

Volatilization of Chemicals from the Open Surface of MHC Tanks. Most plating tanks have a free liquid surface from which chemicals can volatilize into the workplace air. Air currents across the tank will accelerate the rate of volatilization. The EPA's Chemical Engineering Branch (CEB) Manual (EPA, 1991a) suggests the following model for evaporation of chemicals from open surfaces:

$$F_{y,o} = 1200 c_{L,y} H_y A [D_{y,air} v_z / (\pi z)]^{0.5}$$

where:

 $F_{y,o}$ = volatilization rate of chemical y from open tanks (mg/min)

 c_{Ly} = concentration of chemical y in bulk liquid (mg/L)

H_y = dimensionless Henry's Law Constant (H_c) for chemical y D_{v.air} = molecular diffusion coefficient of chemical y in air (cm²/sec)

 v_z = air velocity (m/sec)

z = distance along the pool surface (m)

A = bath area (m^2)

Some limitations of the model should be pointed out. The model was developed to predict the rate of volatilization of pure chemicals, not aqueous solutions. The model was also derived using pure chemicals. As a result, the model implicitly assumes that mass transfer resistance on the gas side is the limiting factor. The model may overestimate volatilization of chemicals from solutions when liquid-side mass transfer is the controlling factor.

Calculation of Chemical Concentration in Workplace Air from Emission Rates. The indoor air concentration is estimated from the following equation (EPA, 1991a):

$$C_v = F_{v,T}/(V_R R_V k)$$

where:

 C_{ν} = workplace contaminant concentration (mg/m³)

 F_{vT} = total emission rate of chemical from all sources (mg/min)

 $V_R^{(1)}$ = room volume (m³)

R_V = room ventilation rate (min⁻¹) k = dimensionless mixing factor

The mixing factor accounts for slow and incomplete mixing of ventilation air with room air. A value of 1.0 was used for this factor. The CEB Manual commonly uses values of the ventilation rate Q from 500 ft³/min to 3,500 ft³/min. Ventilation rates for MHC lines were determined from the facility data. An air turnover rate of 0.021 per minute (1.26 per hour) was used, which is based on estimated air turnover rates that yield 90th percentile air concentrations from Monte Carlo analysis. (This is explained in detail in Appendix D.) An average room volume was used from questionnaire data assuming a ten foot room height.

Other assumptions pertaining to these air models include the following:

- Deposition on equipment, condensation of vapors, and photodegadation are negligible.
- Incoming air is contaminant-free.
- The concentration of contaminant at the beginning of the day is zero.
- As much air enters the room as exits through ventilation (mass balance).
- Room air and ventilation air mix ideally.

Sensitivity Analysis. Model sensitivity and uncertainty was examined using Monte Carlo analysis with the air transport equations outlined above and probability distributions for each parameter based on data from the IPC Workplace Practices Questionnaire (see Appendix D for details). This was done with a Monte Carlo software package (Crystal BallTM [Decisioneering, Inc., 1993]) in conjunction with a spreadsheet program.

This analysis suggested that a few parameters are key to modeling chemical flux from PWB tanks. These key parameters are air turnover rate, bath temperature, chemical concentration in the bath, and Henry's Law Constant.

The air model's sensitivity to these parameters and their uncertainty provides a means of isolating them from less important variables. Isolating these variables allows for additional

scrutiny to be placed upon the point estimate assumptions used for them in the volatilization models.

The air turnover rate assumption contributes most to overall model variance. The chemical bath concentration and bath temperature also contribute variance to the model, but are less important than air turnover rate. This statement is fortified by the fact that relatively accurate information is available on their distributions. $H_{\rm C}$ appears to be least important of the four, but may have more variability associated with it. The models appear to be largely indifferent to small changes in most other parameters.

Modeling Air Concentrations for Population Exposure

The following approach was used for dispersion modeling of air emissions from a single facility:

- Model: Industrial Source Complex Long Term ISC(2)LT model from the Risk*AssistantTM software.
- Building (release) height: 3m.
- Area source: 10 x 10 m.
- Meteorological data: an average emission rate-to-air concentration factor of 2.18 x 10⁻⁶ min/m³ was determined using data for Oakland, California; Denver, Colorado; and Phoenix, Arizona. (These three areas give the highest modeled concentrations around a facility for any available city data in the model.)
- Other parameters: regulatory default values were used. (These are model defaults pertaining to plume rise, stack-tip downwash, buoyancy-induced dispersion, wind profile exponents, vertical temperature gradient, and buildings adjacent to the emission source.)
- Setting: urban mode. (The setting can be either rural or urban. The urban setting is appropriate for urban areas or for large facilities.)
- Chemical degradation in air: not included in modeling.
- Location for exposure point concentrations: a standard polar grid³ with 36 vector directions and one distance ring (at 100m) was used; the highest modeled air concentration in any direction at 100 meters was used to estimate population exposure.

Because of the short time expected for chemical transport to nearby residents, chemical degradation is not taken into account. The emission rates calculated for workplace inhalation exposures are used for the source emission rates to ambient air. Ambient air concentrations were not modeled for those chemicals with facility emission rates less than 23 kg/year (44 mg/min), with the exception of formaldehyde, which was included because it is a potential carcinogen. Results of ambient air modeling are presented in Table 3.10. Proprietary chemical results are not presented to protect proprietary chemical identities.

³ A polar grid is a coordinate system that describes the location of a point by means of direction and distance in relation to a central point (e.g., two miles northeast of the center). In the model, a series of regularly-spaced concentric distance rings are defined at chosen intervals along with a defined number of direction vectors (e.g., north, south, east, west, northeast, northwest, southeast, and southwest would be eight directions).

Table 3.10 Results of Ambient Air Modeling

Chemical ^a	Emission Rate ^b (mg/min)	Air Conc. (mg/m³)
Electroless Copper, non-conveyorized		
2-Ethoxyethanol	1.46e+03	3.17e-03
Formaldehyde	1.37e+01	3.00e-05
Isopropyl Alcohol; or 2-Propanol	5.24e+02	1.14e-03
Methanol	2.31e+02	5.03e-04
Electroless Copper, conveyorized		
2-Ethoxyethanol	1.55e+03	3.38e-03
Formaldehyde	3.66e+01	7.97e-05
Formic Acid	7.90e+01	1.72e-04
Isopropyl Alcohol; or 2-Propanol	1.04e+03	2.26e-03
Methanol	4.28e+02	9.34e-04
Non-Formaldehyde Electroless Copper, non-	conveyorized	
Isopropyl Alcohol; or 2-Propanol	7.34e+01	1.60e-04
Tin-Palladium, non-conveyorized		
Isopropyl Alcohol; or 2-Propanol	2.94e+02	6.42e-04
Tin-Palladium, conveyorized		_
Ethanolamine	5.23e+01	1.14e-04
Isopropyl Alcohol; or 2-Propanol	2.34e+02	5.11e-04

^a Proprietary chemical results are not presented in order to protect proprietary chemical identities.

Surface Water

Environmental releases to surface water were not quantified because chemical constituents and concentrations in wastewater could not be adequately characterized for the MHC line alone. This is because PWB manufacturers typically combine wastewater effluent from the MHC process line with effluent from other PWB manufacturing processes prior to on-site wastewater pretreatment. The pretreated wastewater is then discharged to a POTW. Many PWB manufacturers measure copper concentrations in effluent from on-site pretreatment facilities in accordance with POTW discharge permits, but they do not measure copper concentrations in MHC line effluent prior to pretreatment. Because there are many sources of coppercontaminated wastewater in PWB manufacturing, the contribution of the MHC line to overall copper discharges could not be estimated. Furthermore, most of the MHC alternatives contain copper, but because these technologies are only now being implemented in the U.S., their influence on total copper discharges from a PWB facility cannot be determined. Finally, while data are available on copper discharges from PWB facilities, data are not available for some of the other metals found in alternatives to electroless copper. Although ecological hazards are assessed in Section 3.3, without exposure or release data ecological risk could not be addressed

b Only those chemicals with an emission rate at least 23 kg/year (44 mg/min), plus formaldehyde, are listed. Carbon, conductive polymer, graphite, and organic-palladium had no modeled emission rates above this cut-off. Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the "x 10^x" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as 1.2 x 10⁻⁴, which is the same as 0.00012 in common decimal notation.

in the risk characterization.

3.2.4 Exposure Parameters and Potential Dose Rate Models

This section contains information on models and parameter values for workplace and population exposure estimates. First, more detailed data from the IPC Workplace Practices Questionnaire are presented, then the exposure models and parameter values used in those models are described.

Workplace Exposure Parameter Values

Data on the frequency and duration of activities indicate the amount of time a worker may be exposed through workplace activities. Questionnaire data pertaining to various worker activities follow.

Line Operation. The time per shift that an MHC line operates gives an indication of the daily exposure duration associated with line operation. Time per shift varies by process type and degree of automation. It is probably also influenced by the total amount of PWB processed at a facility and MHC line capacity. Because limited data do not allow differentiation between MHC line operation needs for the various process alternatives, the same period of time for line operation is assumed for all process alternatives. This time, for all processes, ranges from one to 12 hours per shift, with an average of 6.8 hours per shift and a 90th percentile value of eight hours per shift.

Chemical Bath Sampling. Table 3.11 presents questionnaire data pertaining to duration and frequency of chemical bath sampling. These parameters are assumed to vary by MHC technology, but not by equipment configuration (e.g., non-conveyorized or conveyorized).

Chemical Additions. Table 3.12 presents questionnaire and supplier data pertaining to duration and frequency of chemical additions. Duration data indicate the amount of time a worker may be exposed to the chemicals being added to the bath. Although duration data vary by process and bath type, greater variation may be due to differences in facility operating procedures than differences inherent to process alternatives. Therefore, the same duration is assumed for all facilities, regardless of process, equipment, or bath type. Frequency of chemical additions was determined from supplier-provided data, typically a supplier's Product Data Sheet, which recommends a schedule for chemical additions based on time, amount of PWB (ssf) processed, or bath concentrations determined through sampling. For the purposes of this assessment, schedules based on time or ssf of PWB processed were used.

Chemical Bath Replacement. Table 3.13 presents questionnaire data pertaining to duration of chemical bath replacement. Questionnaire data were combined regardless of process configuration for replacement duration. Bath replacement frequency for conveyorized lines was determined specifically for type of bath. The 90th percentile frequencies are presented in Table 3.14.

Table 3.11 Duration and Frequency of Chemical Bath Sampling

Process Alternative (number responding) ^a	Duration of Sampling (minutes)		Frequency of Sampling (occur./year)		Total Responses for
	Average ^b	90th Percentile	Average ^b	90th Percentile	All Baths
Electroless Copper (32)	0.44 - 5.4	3	217 - 996	720	212
Carbon (2)	2.0	2	220	220	8
Conductive Polymer (1)	1.0	1	100 - 460	414	3
Graphite (4)	1.0 - 5.5	10	213 - 255	260	13
Non-Formaldehyde Electroless Copper (1)	1.0	1	50 - 260	260	5
Organic-Palladium (2)	1.5 - 2	2	230 - 490	250	13
Tin-Palladium (12)	1.2 - 4.0	2	210 - 660	520	65

^a Five facilities did not respond to this question.

Table 3.12 Duration and Frequency of Chemical Additions

Facility Type	Duration of Chemica (minutes)	Frequency of Chemical	
	Average 90th Percentile		Additions (times/year) ^b
Electroless Copper	3.6 - 10 ^c	ND	0.4 - 52°
Carbon	2 - 10°	ND	1 - 58°
Graphite	2 - 19°	ND	4 - 44 ^c
Non-Formaldehyde Electroless Copper	2, regardless of bath type	ND	
Organic-Palladium	20 - 25°	ND	11 - 52°
Tin-Palladium	5 - 15°	ND	0.7 - 12°
All Facilities, regardless of process type	8.6	20	ND

^a From IPC Workplace Practices Questionnaire and Performance Demonstration database.

ND: Not Determined.

Table 3.13 Duration of Chemical Bath Replacement

Process Alternative	Duration (minutes)			
(number responding)	Average ^a	90th Percentile	Total Responses for All Baths	
Electroless Copper (36)	41 - 147	180	205	
Carbon (2)	15 - 180	180	8	
Conductive Polymer (1)	60 - 240	228	3	
Graphite (3)	18 - 240	219	10	
Non-Formaldehyde Electroless Copper (1)	30	30	5	
Organic-Palladium (2)	30 - 360	108	13	
Tin-Palladium (13)	31 - 110	180	75	
All Facilities	78	ND	350	

^a Range of averages for each bath type.

ND: Not Determined.

^b Range of averages for each bath type.

^b Based on supplier-provided information.

^c Depending on bath type.

Table 3.14 Frequency of Chemical Bath Replacement for Conveyorized Processes

Process Alternative	Bath Type	90th Percentile	Bath Type	90th Percentile
1 Tocess Atternative	Dain Type		Dath Type	
		Frequency		Frequency
		(occur./year)		(occur./year)
Electroless Copper	Conditioner/Cleaner	24	Accelerator	16
	Microetch	50	Electroless	4
	Predip	24	Copper	50
	Catalyst	1	Acid Dip	28
			Anti-Tarnish	
Carbon	Cleaner	30	Carbon Black	1
	Conditioner	30	Microetch	145
Conductive Polymer	Microetch	20.5	Catalyst	1
	Cleaner/Conditioner	13	Conductive	17
			Polymer	
Graphite	Cleaner/Conditioner	56	Microetch	145
	Graphite	7.3		
Organic-Palladium	Conditioner	32	Conductor	1
	Microetch	1	Post-Dip	20
	Predip	230	•	
Tin-Palladium	Cleaner/Conditioner	141	Accelerator	47
	Predip	151	Microetch	65
	Catalyst	1	Acid Dip	230

Conveyor Equipment Cleaning. For conveyor equipment cleaning, nine facilities responded out of a total of 11 conveyorized systems. For these facilities:

- Duration of conveyor equipment cleaning ranged from 0.5 to 480 minutes, with an average of 140 minutes and 90th percentile of 288 minutes.
- Frequency of conveyor equipment cleaning ranged from two to 260 times per year, with an average of 55 times per year and 90th percentile of 92 times per year.

Bath Filter Replacement. Table 3.15 presents data on duration and frequency of bath filter replacement. For filter replacement, depending on bath and process types, the average duration ranges from one to 31 minutes and the average frequency ranges from 12 to 300 times per year. The frequency data used for intake model parameters is process-specific. Again, the duration for all facilities is assumed, regardless of process alternative or bath type.

Working in the Process Area. Table 3.16 presents questionnaire data pertaining to the amount of time various types of workers spend working in the MHC process area. Frequency is considered to be the days/year the MHC line is in operation (an average of 250 days/year and 90th percentile of 306 days/year).

Table 3.15 Filter Replacement

Process Alternative (number responding) ^a	Duration (minutes)		Total Responses	Frequency (occur./year)		Total Responses
	Average ^b	90th Percentile	for All Baths	Average ^b	90th Percentile	for All Baths
Electroless Copper (20)	8 - 31	ND	82	37 - 200	100	76
Carbon (2)	5	ND	6	12 - 20	20	6
Conductive Polymer (1)	5 - 10	ND	4	12.5 - 115	74	4
Graphite (4)	7 - 10	ND	9	67 - 107	103	9
Non-Formaldehyde Electroless Copper (1)	1 - 5	ND	2	16.7	17	2
Organic-Palladium (2)	2 - 3.5	ND	10	12 - 38	50	10
Tin-Palladium (3)	5 - 11	ND	14	24 - 300	74	14
All Facilities	13	20	138	ND	ND	138

 ^a Sixteen facilities did not respond to this question.
 ^b Range of averages for each bath type.

ND: Not Determined.

Table 3.16 Duration of Working in the Process Area

Worker Type	Range (hours/shift)	Average (hours/shift)	90th Percentile (hours/shift)
Line Operators	3.3 - 10	7.8	8
Laboratory Technicians	0.1 - 10	3.9	8
Maintenance Workers	0.15 - 10	3.1	8
Supervisory Personnel	0.23 - 10	4.7	8
Wastewater Treatment Operators	0.1 - 10	4.4	8
Contract Workers	0.25	0.25	0.25
Other Employees	0.18 - 8	3.4	5.6

Workplace Exposure Models

The general models for calculating inhalation and dermal potential dose rates are discussed below.

Daily Inhalation Exposures. The general model for inhalation exposure to workers is from CEB (EPA, 1991a):

$$I = (Cm)(b)(h)$$

where:

Ι = daily inhalation potential dose rate (mg/day)

= airborne concentration of substance (mg/m³) (note: this term is denoted "C_v" in

air modeling equation in Section 3.2.3)

= inhalation rate (m³/hr) b

= duration (hr/day) h

Data for these parameters are in Table 3.17.

Table 3.17 Parameter Values for Daily Workplace Inhalation Exposures

Parameter	Units	Value	Source of Data, Comments	
Cm	mg/m ³	Modeled from single or average bath concentrations		
b	m ³ /hr	1.25	EPA, 1991a (data from NIOSH, 1976).	
Duration (h)				
Line Operation	hours/day	8	From IPC Workplace Practices Questionnaire, 90th percentile for hours of MHC line operation, all process types (assuming hours/shift = hours/day).	
Working in Process Area	hours/day	8	From IPC Workplace Practices Questionnaire, 90th percentile for hours/shift for first shift, all process types.	

Daily Workplace Dermal Exposures. The general model for potential dose rate via dermal exposure to workers is from CEB (EPA, 1991a):

$$D = SQC$$

where:

D = dermal potential dose rate (mg/day)

S = surface area of contact (cm²)

Q = quantity typically remaining on skin (mg/cm²)

C = concentration of chemical (percent)

Because a line operator is expected to have dermal contact with the chemicals in a given bath several times a day in the course of normal operations, the total time of contact combined with a flux rate (rate of chemical absorption through the skin) is believed to give a more realistic estimate of dermal exposure. The flux of a material through the skin is estimated in terms of mg absorbed per cm² per unit of time. Using flux of material through the skin, (based on EPA, 1992a) the equation is modified to:

$$D = (S)(C)(f)(h)(0.001)$$

where:

D = dermal potential dose rate (mg/day)

S = surface area of contact (cm²)

C = concentration of chemical (mg/L)

f = flux through skin (cm/hour)

h = duration (hours/day)

with a conversion factor of 0.001 L/cm³

This second equation was used for all workplace dermal exposure estimates.

Data for duration of contact (h) from the IPC Workplace Practices Questionnaire are included in Table 3.18.

 Table 3.18 Parameter Values for Daily Workplace Dermal Exposures

Parameter	Units	Value		Source of Data, Comments
			and are 1 ·	,
С	%		disclosed proprie	ermined from publicly-available etary ingredient information (see
S	cm ²	1,300		CEB Table 4-13, routine immersion, 2 hands, assuming gloves not worn.
Flux Through Skin (f)	cm/hr	Default for inorganics: 0 estimate for organics by: $\log f = -2.72+0.71 \log K_o$ ($K_{ow} = octanol/water part$	_w -0.0061(MW)	EPA, 1992a.
		coefficient, MW = molec		
Duration of C	Contact (h)			
Line Operation	hours/day			90th percentile from IPC Workplace Practices Questionnaire, hours of MHC line operation, all process types excluding conveyorized processes.
		electroless copper (19 baths) non-formaldehyde electroless copper	0.42	Corrected for typical number of baths in a process, including rinse baths.
		(17 baths) organic-palladium	0.47	
		(12 baths) tin-palladium	0.67	
		(14 baths)	0.57	
Chemical Bath	min/occur	carbon conductive polymer	180 228	90th percentile from IPC Workplace Practices Questionnaire.
Replacement		electroless copper graphite non-formaldehyde	180 219	
		electroless copper organic-palladium tin-palladium	30 108 180	
Conveyor Equipment Cleaning	min/occur	288		90th percentile from IPC Workplace Practices Questionnaire, conveyorized lines.
Filter Replacement	min/occur	20		90th percentile from IPC Workplace Practices Questionnaire, all process types.
Chemical Bath Sampling	min/occur	carbon conductive polymer electroless copper graphite non-formaldehyde electroless copper organic-palladium tin-palladium	2 1 5 10 1 2 2	90th percentile from IPC Workplace Practices Questionnaire, excluding automated sampling.

Daily exposures are averaged over a lifetime (70 years) for carcinogens, and over the exposure duration (e.g., 25 years working in a facility) for non-carcinogens⁴ using the following equations. To estimate average daily doses for inhalation:

```
LADD = (I)(EF)(ED)/[(BW)(AT_{CAR})]

ADD = (I)(EF)(ED)/[(BW)(AT_{NC})]
```

where:

LADD = lifetime average daily dose (mg/kg-day) (for carcinogens)

ADD = average daily dose (mg/kg-day) (for non-carcinogens)

I = daily inhalation potential dose rate (mg/day)

EF = exposure frequency (days/year)

ED = exposure duration (years)

BW = body weight (kg)

 AT_{CAR} = averaging time for carcinogenic effects (days) AT_{NC} = averaging time for non-carcinogenic effects (days)

To estimate average daily doses from dermal contact:

```
LADD = (D)(EF)(ED)/[(BW)(AT_{CAR})]
ADD = (D)(EF)(ED)/[(BW)(AT_{NC})]
```

where:

D = dermal potential dose rate (mg/day)

Parameter values for estimating worker's potential dose rates are presented in Table 3.19. Results of estimating inhalation and dermal ADDs (and the inhalation LADD for formaldehyde) are presented in Table 3.20 and Appendix E. Proprietary chemical results are not presented in order to protect proprietary chemical identities. The frequency data for activities pertaining to operating an MHC line could apply to more than one line worker, although they are assumed here to apply to a single, typical line operator. For example, facilities reported from one to 18 line operators working at one time, with an average of three line operators working the first shift. Therefore, the frequency of various worker activities pertaining to a single line operator may be overestimated by about a factor of three.

⁴ Different averaging times are used for characterizing risk for carcinogenic and non-carcinogenic effects. For carcinogenic agents, because even a single incidence of exposure is assumed to have the potential to cause cancer throughout an individual's lifetime, the length of exposure to that agent is averaged over a lifetime. An additional factor is that the cancer latency period may extend beyond the period of working years before it is discernible. For chemicals exhibiting non-cancer health effects from chronic (longer-term) exposure, where there is an exposure threshold (a level below which effects are not expected to occur); only the time period when exposure is occurring is assumed to be relevant and is used as the averaging time.

Table 3.19 Parameter Values for Estimating Average Workplace Exposures(for line operators)

		(for line oper	ators)				
Parameter	Units	Value		Source of Data, Comments			
Exposure Frequency (EF): Inhalation Exposure							
Line Operation & Working in Process Area	days/year	306		90th percentile, days/year MHC line operates from IPC Workplace Practices Questionnaire, all process types (average is 250 days/year).			
EF: Dermal Exposur	re						
Line Operation	days/year	306		90th percentile, days/year MHC line operates from IPC Workplace Practices Questionnaire, all process types.			
Chemical Bath Replacement	occur/year	electroless copper carbon conductive polymer graphite organic-palladium tin-palladium	1 - 50 1 - 145 1 - 20.5 7.3 - 145 1 - 230 1 - 230	90th percentiles for conveyorized processes from IPC Workplace Practices Questionnaire (see Table 3.14).			
Conveyor Equipment Cleaning	occur/year	92		90th percentile from IPC Workplace Practices Questionnaire, for conveyorized lines.			
Filter Replacement	occur/year	electroless copper carbon conductive polymer graphite non-formaldehyde electroless copper organic-palladium tin-palladium	100 20 74 103 17 50 74	90th percentiles from IPC Workplace Practices Questionnaire.			
Chemical Bath Sampling	occur/year	electroless copper carbon conductive polymer graphite non-formaldehyde electroless copper organic-palladium tin-palladium	720 220 414 260 260 250 520	90th percentiles from IPC Workplace Practices Questionnaire, excluding automated sampling.			
Parameters Pertainii	ng to All Wo	orkplace Exposures (for Line O	perators)			
Exposure Duration (ED)	years	25		95th percentile for job tenure (Bureau of Labor Statistics, 1990). (Median tenure for U.S. males is 4 years; Bureau of Labor Statistics, 1997.)			
Body Weight (BW)	kg	70		Average for adults (EPA, 1991b).			
Averaging Time (AT) AT_{CAR} AT_{NC}	days	25,550 9,125		70 yrs (average lifetime)*365 d/yr 25 yrs (ED)*365 d/yr			

Table 3.20 Estimated Average Daily Dose (ADD) for Workplace Exposure - Inhalation and Dermal

Inhalation and Dermal					
Chemical ^a		ADD			
	Inhalation	(mg/kg-day	Dermal		
	Line Operator	Line Operator	Laboratory Technician		
Electroless Copper, non-conveyorized		-			
Ammonium Chloride	NA	8.4e-02	2.1e-03		
Benzotriazole	6.64e-04	2.5e-03	6.1e-05		
Boric Acid	9.15e-04	3.3e-02	8.0e-04		
Copper (I) Chloride	4.05e-04	4.4e-02	1.1e-03		
Copper Sulfate; or Cupric Sulfate	4.45e-04	4.9e-02	1.2e-03		
Dimethylaminoborane	1.04e-02	3.9e-03	9.6e-05		
Dimethylformamide	7.58e-03	1.1e-03	2.8e-05		
Ethanolamine	5.31e-02	1.0e-02	2.5e-04		
2-Ethoxyethanol	7.79e+00	1.4e-01	3.4e-03		
Ethylene Glycol	1.78e-02	2.5e-03	6.0e-05		
Ethylenediaminetetraacetic Acid (EDTA)	2.74e-03	1.7e-05	4.2e-07		
Fluoroboric Acid	1.18e-02	3.9e-01	9.6e-03		
Formaldehyde	7.36e-02	1.1e-02	2.6e-04		
Formaldehyde (LADD) ^b	2.63e-02	NA	NA		
Formic Acid	1.88e-01	3.5e-02	8.5e-04		
Hydrochloric Acid	2.91e-05	9.0e-01	2.2e-02		
Hydrogen Peroxide	8.87e-04	1.3e-01	3.2e-03		
Hydroxyacetic Acid	1.68e-04	2.4e-02	5.9e-04		
Isopropyl Alcohol; or 2-Propanol	2.81e+00	3.1e-02	7.7e-04		
Magnesium Carbonate	5.35e-05	7.8e-03	1.9e-04		
Methanol	1.24e+00	1.1e-02	2.8e-04		
m-Nitrobenzene Sulfonic Acid	4.90e-06	8.8e-07	2.2e-08		
p-Toluene Sulfonic Acid	NA	4.0e-03	9.8e-05		
Palladium	NA	2.4e-03	5.8e-05		
Peroxymonosulfuric Acid	1.15e-03	1.7e-01	4.2e-03		
Potassium Bisulfate	6.15e-04	9.0e-02	2.2e-03		
Potassium Cyanide	1.35e-05	1.5e-03	3.6e-05		
Potassium Hydroxide	1.25e-05	5.4e-03	1.3e-04		
Potassium Persulfate	4.37e-04	6.4e-02	1.6e-03		
Potassium Sulfate	8.56e-04	1.3e-01	3.1e-03		
Potassium-Sodium Tartrate	1.90e-03	2.1e-01	5.0e-03		
Sodium Bisulfate	NA	4.6e-01	1.1e-02		
Sodium Carbonate	3.03e-06	3.3e-04	8.03-06		
Sodium Chlorite	NA	3.0e-02	7.2e-04		

Chemical ^a		ADD (mg/kg-day)			
	Inhalation	De	ermal		
	Line Operator	Line Operator	Laboratory Technician		
Sodium Cyanide	1.40e-05	1.5e-03	3.7e-05		
Sodium Hydroxide	6.30e-04	8.5e-02	2.1e-03		
Sodium Hypophosphite	NA	5.6e-02	1.4e-03		
Sodium Sulfate	NA	8.3e-02	2.0e-03		
Stannous Chloride	NA	6.7e-02	1.6e-03		
Sulfuric Acid	6.67e-03	1.2e+00	2.9e-02		
Tartaric Acid	6.24e-05	5.7e-05	1.4e-06		
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	NA	3.5e-03	8.5e-05		
Electroless Copper, conveyorized					
Ammonium Chloride	NA	2.1e-02	2.1e-03		
Benzotriazole	NA	6.3e-04	6.1e-05		
Boric Acid	NA	9.2e-03	8.0e-04		
Copper (I) Chloride	NA	9.8e-03	1.1e-03		
Copper Sulfate; or Cupric Sulfate	NA	1.1e-02	1.2e-03		
Dimethylaminoborane	NA	1.1e-03	9.6e-05		
Dimethylformamide	NA	2.8e-04	2.8e-05		
Ethanolamine	NA	2.5e-03	2.5e-04		
2-Ethoxyethanol	NA	3.5e-02	3.4e-03		
Ethylene Glycol	NA	6.5e-04	6.0e-05		
Ethylenediaminetetraacetic Acid (EDTA)	NA	3.8e-06	4.2e-07		
Fluoroboric Acid	NA	9.4e-02	9.6e-03		
Formaldehyde	NA	2.4e-03	2.6e-04		
Formic Acid	NA	8.6e-03	8.5e-04		
Hydrochloric Acid	NA	2.1e-01	2.2e-02		
Hydrogen Peroxide	NA	3.6e-02	3.2e-03		
Hydroxyacetic Acid	NA	6.0e-03	5.9e-04		
Isopropyl Alcohol; or 2-Propanol	NA	7.8e-03	7.7e-04		
Magnesium Carbonate	NA	2.2e-03	1.9e-04		
Methanol	NA	2.6e-03	2.8e-04		
m-Nitrobenzene Sulfonic Acid	NA	2.2e-07	2.2e-08		
p-Toluene Sulfonic Acid	NA	9.9e-04	9.8e-05		
Palladium	NA	5.2e-04	5.8e-05		
Peroxymonosulfuric Acid	NA	4.7e-02	4.2e-03		
Potassium Bisulfate	NA	2.5e-02	2.2e-03		
Potassium Cyanide	NA	3.3e-04	3.6e-05		
Potassium Hydroxide	NA	1.4e-03	1.3e-04		

Chemical ^a		ADD (mg/kg-day)			
	Inhalation		ermal		
	Line Operator	Line Operator	Laboratory Technician		
Potassium Persulfate	NA	1.8e-02	1.6e-03		
Potassium Sulfate	NA	3.5e-02	3.1e-03		
Potassium-Sodium Tartrate	NA	4.6e-02	5.0e-03		
Sodium Bisulfate	NA	1.0e-01	1.1e-02		
Sodium Carbonate	NA	7.3e-05	8.0e-06		
Sodium Chlorite	NA	7.0e-03	7.2e-04		
Sodium Cyanide	NA	3.4e-04	3.7e-05		
Sodium Hydroxide	NA	1.9e-02	2.1e-03		
Sodium Hypophosphite	NA	1.3e-02	1.4e-03		
Sodium Sulfate	NA	1.8e-02	2.0e-03		
Stannous Chloride	NA	1.5e-02	1.6e-03		
Sulfuric Acid	NA	3.2e-01	2.9e-02		
Tartaric Acid	NA	1.3e-05	1.4e-06		
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	NA	8.6e-04	8.5e-05		
Carbon, conveyorized					
Copper Sulfate; or Cupric Sulfate	NA	1.7e-02	1.4e-04		
Ethanolamine	NA	9.6e-03	1.3e-04		
Potassium Hydroxide	NA	7.3e-02	1.2e-03		
Sodium Persulfate	NA	7.0e-01	5.7e-03		
Sulfuric Acid	NA	6.4e-03	5.3e-05		
Conductive Polymer, conveyorized					
1H-Pyrrole	NA	2.6e-02	3.3e-04		
Peroxymonosulfuric Acid; or Potassium Peroxymonosulfate	NA	7.0e-01	8.8e-03		
Phosphoric Acid	NA	1.0e-01	1.3e-03		
Sodium Carbonate	NA	2.5e-02	3.3e-04		
Sodium Hydroxide	NA	2.7e-03	4.0e-05		
Sulfuric Acid	NA	1.4e-02	1.8e-03		
Graphite, conveyorized	· ·				
Ammonia	NA	4.2e-03	3.3e-04		
Copper Sulfate; or Cupric Sulfate	NA	1.1e-02	4.5e-04		
Ethanolamine	NA	5.3e-03	3.2e-04		
Graphite	NA	9.8e-02	7.7e-03		
Peroxymonosulfuric Acid; or Potassium Peroxymonosulfate	NA	1.2e-01	5.1e-03		
Potassium Carbonate	NA	2.1e-02	1.3e-03		
Sodium Persulfate	NA	2.4e-01	9.7e-03		
Sulfuric Acid	NA	2.4e-01	1.0e-02		

Chemical ^a		ADD (mg/kg-day)			
	Inhalation		ermal		
	Line Operator	Line Operator	Laboratory Technician		
Non-Formaldehyde Electroless Copper, non-conveyorized					
Copper Sulfate; or Cupric Sulfate	1.47e-03	1.7e-01	2.7e-04		
Hydrochloric Acid	NA	2.2e-02	3.4e-05		
Hydrogen Peroxide	5.01e-04	1.2e-01	1.9e-04		
Isopropyl Alcohol; or 2-Propanol	3.93e-01	1.3e-02	2.1e-05		
Potassium Hydroxide	7.99e-06	2.2e-03	3.5e-06		
Potassium Persulfate	3.04e-04	7.2e-02	1.1e-04		
Sodium Chlorite	NA	3.3e-02	5.2e-05		
Sodium Hydroxide	9.31e-06	2.2e-03	3.5e-06		
Stannous Chloride	NA	6.9e-02	1.1e-04		
Sulfuric Acid	7.94e-04	1.7e-01	2.6e-04		
Organic-Palladium, non-conveyorized	<u>u</u>				
Hydrochloric Acid	NA	6.4e-02	2.2e-04		
Sodium Bisulfate	NA	7.8e-01	2.7e-03		
Sodium Carbonate	NA	2.3e-01	7.8e-04		
Sodium Hypophosphite	NA	3.2e-02	1.1e-04		
Sodium Persulfate	NA	7.8e-01	2.7e-03		
Trisodium Citrate 5.5-Hydrate; or Sodium Citrate	NA	6.7e-03	2.3e-05		
Organic-Palladium, conveyorized	•				
Hydrochloric Acid	NA	1.8e-02	2.2e-04		
Sodium Bisulfate	NA	1.5e-01	2.6e-03		
Sodium Carbonate	NA	4.8e-02	7.8e-04		
Sodium Hypophosphite	NA	6.1e-03	1.1e-04		
Sodium Persulfate	NA	1.5e-01	2.6e-03		
Trisodium Citrate 5.5-Hydrate; or Sodium Citrate	NA	1.4e-03	2.3e-05		
Tin-Palladium, non-conveyorized					
1,3-Benzenediol	NA	9.7e-03	9.7e-05		
Copper (I) Chloride	NA	2.3e-02	2.3e-04		
Copper Sulfate; or Cupric Sulfate	3.95e-04	1.3e-01	1.2e-03		
Ethanolamine	1.07e-01	2.7e-02	2.7e-04		
Fluoroboric Acid	9.45e-03	1.7e-01	1.7e-03		
Hydrochloric Acid	NA	2.9e-01	2.9e-03		
Hydrogen Peroxide	5.20e-04	1.6e-01	1.5e-03		
Isopropyl Alcohol; or 2-Propanol	1.58e+00	1.6e-02	1.6e-04		
Lithium Hydroxide	NA	1.8e-01	1.8e-03		
Palladium	NA	8.5e-03	8.5e-05		

Chemical ^a		ADD (mg/kg-day)			
	Inhalation	De	ermal		
	Line	Line	Laboratory		
	Operator	Operator	Technician		
Palladium Chloride	NA	5.3e-03	5.3e-05		
Potassium Carbonate	NA	2.9e+00	2.9e-02		
Sodium Bisulfate	NA	7.9e-01	7.9e-03		
Sodium Chloride	NA	9.0e+00	9.0e-02		
Sodium Hydroxide	NA	2.6e-01	2.6e-03		
Sodium Persulfate	4.49e-03	1.3e+00	1.3e-02		
Stannous Chloride	NA	2.8e-01	2.8e-03		
Sulfuric Acid	6.21e-04	1.9e+00	1.9e-02		
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	NA	2.4e-03	2.4e-05		
Vanillin	4.33e-04	3.0e-03	3.0e-05		
Tin-Palladium, conveyorized					
1,3-Benzenediol	NA	2.7e-03	9.7e-05		
Copper (I) Chloride	NA	8.1e-03	2.3e-04		
Copper Sulfate; or Cupric Sulfate	NA	4.9e-02	1.2e-03		
Ethanolamine	NA	1.2e-02	2.7e-04		
Fluoroboric Acid	NA	6.0e-02	1.7e-03		
Hydrochloric Acid	NA	1.1e-01	2.9e-03		
Hydrogen Peroxide	NA	6.1e-02	1.6e-03		
Isopropyl Alcohol; or 2-Propanol	NA	8.4e-03	1.6e-04		
Lithium Hydroxide	NA	6.5e-02	1.8e-03		
Palladium	NA	2.4e-03	8.5e-05		
Palladium Chloride	NA	1.5e-03	5.3e-05		
Potassium Carbonate	NA	1.0e+00	2.9e-02		
Sodium Bisulfate	NA	3.3e-01	7.9e-03		
Sodium Chloride	NA	3.3e+00	9.0e-02		
Sodium Hydroxide	NA	9.2e-02	2.6e-03		
Sodium Persulfate	NA	5.2e-01	1.3e-02		
Stannous Chloride	NA	7.9e-02	2.8e-03		
Sulfuric Acid	NA	1.2e+00	1.9e-02		
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	NA	1.2e-03	2.4e-05		
Vanillin	NA	8.4e-04	3.0e-05		

^a Proprietary chemical results are not presented in order to protect proprietary chemical identities.

Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the

NA: Not Applicable. A number was not calculated because the chemical's vapor pressure is below the 1×10^{-3} torr cutoff and is not used in any sparged bath. Inhalation exposures are therefore expected to be negligible. LADDs were not calculated for dermal exposure.

^b LADD is calculated using a carcinogen averaging time (AT_{CAR}) of 70 years.

[&]quot; \times 10" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as 1.2 x 10⁻⁴, which is the same as 0.00012 in common decimal notation.

Population Exposure

The equation for estimating ADDs from inhalation for a person residing near a facility is:

$$\begin{split} LADD &= (Ca)(IR)(EF)(ED)/[(BW)(AT_{CAR})] \\ ADD &= (Ca)(IR)(EF)(ED)/[(BW)(AT_{NC})] \end{split}$$

where:

LADD = lifetime average daily dose (mg/kg-day) (for carcinogens)

ADD = average daily dose (mg/kg-day) (for non-carcinogens)

Ca = chemical concentration in air (mg/m^3) (from air dispersion modeling, described

in Section 3.2.3)

IR = inhalation rate (m³/day) EF = exposure frequency (day/yr) ED = exposure duration (years) BW = average body weight (kg)

 AT_{CAR} = averaging time for carcinogenic effects (days)

 AT_{NC} = averaging time for non-carcinogenic chronic effects (days)

Table 3.21 presents values used for these parameters.

Table 3.21 Parameter Values for Estimating Nearby Residential Inhalation Exposure

Parameter	Units	Value	Source of Data, Comments	
Ca	mg/m ³		Modeled, varies by chemical and process type.	
IR	m ³ /day	15	Total home exposures for adults based on activity patterns and inhalation rates (EPA, 1997).	
EF	days/year	350	Assumes 2 weeks per year spent away from home (EPA, 1991b).	
ED	years	30	National upper 90th percentile at one residence (EPA, 1990).	
BW	kg	70	Average value for adults (EPA, 1991b).	
AT	days			
AT_{CAR}			70 yrs*365 days/year	
AT_{NC}		10,950	ED * 365 days/year	

Results for general population inhalation exposure are presented in Table 3.22 and Appendix E. Proprietary chemical results are not presented in order to protect proprietary chemical identities.

Table 3.22 Estimated Average Daily Dose (ADD) for General Population Inhalation Exposure

Chemical ^a	ADD (mg/kg-day)
Electroless Copper, non-conveyorized	
2-Ethoxyethanol	6.5e-04
Formaldehyde	7.4e-06
Formaldehyde (LADD) ^b	2.6e-06
Isopropyl Alcohol; or 2-Propanol	2.4e-04
Methanol	1.0e-04
Electroless Copper, conveyorized	
2-Ethoxyethanol	7.0e-04
Formaldehyde	2.0e-05
Formaldehyde (LADD) ^b	7.0e-06
Formic Acid	3.5e-05
Isopropyl Alcohol; or 2-Propanol	4.6e-04
Methanol	1.9e-04
Non-Formaldehyde Electroless Copper, non-conveyoriz	zed
Isopropyl Alcohol; or 2-Propanol	3.3e-05
Tin-Palladium, non-conveyorized	·
Isopropyl Alcohol; or 2-Propanol	1.3e-04
Tin-Palladium, conveyorized	
Ethanolamine	2.3e-05
Isopropyl Alcohol; or 2-Propanol	1.0e-04

^a Only those chemicals with an emission rate at least 23 kg/year (44 mg/min), plus formaldehyde, are listed. Carbon, conductive polymer, graphite, and organic-palladium had no modeled emission rates above this cut-off. Also, proprietary chemical results are not presented in order to protect proprietary chemical identities.

Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the " \times 10" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as 1.2 \times 10⁻⁴, which is the same as 0.00012 in common decimal notation.

3.2.5 Uncertainty and Variability

Because of both the uncertainty inherent in the parameters and assumptions used in estimating exposure, and the variability that is possible within a population, there is no one number that can be used to describe exposure. In addition to data and modeling limitations, discussed in Sections 3.2.3, sources of uncertainty in assessing exposure include the following:

Accuracy of the description of exposure setting: how well the model facility used in the
assessment characterizes an actual facility; the likelihood of exposure pathways actually
occurring (scenario uncertainty).

^b LADD is calculated using a carcinogen averaging time (AT_{CAR}) of 70 years.

- Missing data and limitations of workplace practices data: this includes possible effects of any chemicals that may not have been included (e.g., minor ingredients in the formulations and proprietary chemical identities not disclosed by suppliers⁵); possible effects of side reactions in the baths, which were not considered; and questionnaire data with limited facility responses.
- Estimating exposure levels from averaged data and modeling in the absence of measured, site-specific data.
- Data limitations in the Source Release Assessment: releases to surface water and land could not be characterized quantitatively, as discussed in Section 3.1.
- Chemical fate and transport model applicability and assumptions: how well the models and assumptions represent the situation being assessed and the extent to which the models have been validated or verified (model uncertainty).
- Parameter value uncertainty, including measurement error, sampling error, parameter variability, and professional judgement.
- Uncertainty in combining pathways for an exposed individual.

A method typically used to provide information about the position an exposure estimate has in the distribution of possible outcomes is the use of exposure (or risk) descriptors. EPA's *Guidelines for Exposure Assessment* (EPA, 1992b) provides guidance on the use of risk descriptors, which include the following:

- *High-end*: approximately the 90th percentile of the actual (measured or estimated) distribution. This is a plausible estimate of individual risk for those persons at the upper end of the exposure distribution, and is not higher than the individual in the population who has the highest exposure.
- *Central tendency*: either an average estimate (based on average values for the exposure parameters) or a median estimate (based on 50th percentile or geometric mean values).
- What-if: represents an exposure estimate based on postulated questions (e.g., what if the air ventilation rates were ...), in this case, making assumptions based on limited data so that the distribution is unknown. If any part of the exposure assessment qualifies as a "what-if" descriptor, then the entire exposure assessment is considered "what-if."

This exposure assessment uses whenever possible a combination of central tendency (either an average or median estimate) and high-end (90th percentile)⁶ assumptions, as would be used for an overall high-end exposure estimate. The 90th percentile is used for:

⁵ Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. Atotech provided information on one proprietary ingredient. W.R. Grace was making arrangements to transfer information on proprietary chemical ingredients in the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Enthone-OMI, MacDermid, and Shipley) declined to provide proprietary information on their MHC technologies. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients is presented in this CTSA, but chemical identities, concentrations, and chemical properties are not listed.

⁶ For exposure data from the IPC Workplace Practices Questionnaire, this means that 90 percent of the facilities reported a lower value, and ten percent reported a higher value.

- Hours per day of workplace exposure.
- Exposure frequency (days per year).
- Exposure duration in years (90th percentile for occupational and 95th percentile for residential exposures).
- The time and frequency of chemical bath and filter replacements, conveyor equipment cleaning and chemical bath sampling (minutes per occurrence and number of occurrences per year), and estimated workplace air concentrations.

Average values are used for:

- Body weight.
- Concentration of chemical in bath.
- The number of baths in a given process.

However, because some data, especially pertaining to bath concentrations and inhalation exposure are limited, and this exposure assessment does not apply to a specific facility, the entire exposure assessment should be considered "what-if."

3.2.6 Summary

This exposure assessment uses a "model facility" approach, with the goal of comparing the exposures and health risks of one MHC technology to the exposures and risks associated with switching to another technology. As much as possible, reasonable and consistent assumptions are used across alternatives. Data to characterize the model facility and exposure patterns for each MHC technology were aggregated from a number of sources, including PWB shops in the U.S. and abroad, supplier data, and input from PWB manufacturers at project meetings. Thus, the model facility is not entirely representative of any one facility, and actual exposure (and risk) could vary substantially, depending on site-specific operating conditions and other factors.

Chemical exposures to PWB workers and the general population from day-to-day MHC line operations were estimated by combining information gathered from industry (IPC Workplace Practices Questionnaire, MSDSs, and other available information) with standard EPA exposure assumptions for inhalation rate, surface area of dermal contact and other parameters, as discussed in the exposure assessment. The pathways identified for potential exposure from MHC process baths were inhalation and dermal contact for workers, and inhalation contact only for the general populace living near a PWB facility.

Environmental releases to surface water were not quantified due to a lack of data and the limited scope of this assessment. Chemical constituents and concentrations in wastewater could not be adequately characterized (see Section 3.2.3). Nor were the possible impacts of short-term exposures to high levels of hazardous chemicals addressed, such as those that could occur from chemical fires, spills, or other periodic releases.

Inhalation exposure could occur by breathing air containing vapor or aerosol-phase chemicals from the MHC process line. Inhalation exposures to workers are estimated only for non-conveyorized lines; inhalation exposure to workers from conveyorized MHC lines was assumed to be negligible because the lines are typically enclosed and vented to the outside.

The daily intake for inhalation exposure to workers was calculated by first modeling chemical emissions from MHC baths with three air-transport mechanisms: liquid surface diffusion (desorption), bubble desorption, and aerosol generation and ejection. This chemical emission rate was combined with information from the IPC Workplace Practices Questionnaire regarding process room size and air turnover rate to estimate an average indoor air concentration for the process area. General room ventilation was assumed, although the majority of shops have local ventilation on chemical tanks. An uncertainty and sensitivity analysis of the air transport models suggests that the air turnover (ventilation) rate assumption greatly influences the estimated air concentration in the process area because of its large variability.

Inhalation exposure to the human population surrounding PWB plants was estimated using the Industrial Source Complex - Long Term (ISCLT) air dispersion model. The modeled air concentrations of each contaminant were determined at 100 meters radially from a PWB facility, and the highest estimated air concentration was used. This model estimates air concentration from the process bath emission rates. These emissions were assumed to be vented to the ambient environment at the rate emitted from the baths, for all process alternatives. Inhalation exposures estimated for the public living 100 meters away from a PWB facility were very low (approximately 10,000 times lower than occupational exposures).

Dermal exposure could occur when skin comes in contact with the bath solution while dipping boards, adding replacement chemicals, etc. Although the data suggest that most MHC line operators do wear gloves, it was assumed in this evaluation that workers do not wear gloves to account for the fraction that do not. Otherwise, dermal exposure is expected to be negligible. For dermal exposure, the concentration of chemical in the bath and duration of contact for workers was obtained from the IPC Workplace Practices Questionnaire information. A permeability coefficient (rate of penetration through skin) was estimated for organics and a default rate assumption was used for inorganics. Another source of uncertainty in dermal modeling lies with the assumed duration of contact. The worker is assumed to have potential dermal contact for the entire time spent in the MHC area, divided equally among the baths. (This does not mean that a worker has both hands immersed in a bath for that entire time; but that the skin is in contact with bath solution, i.e., the hands may remain wet from contact.) This assumption may result in an overestimate of dermal exposure.

Assumptions and parameter values used in these equations are presented throughout this section. Complete results of the exposure calculations are presented in Appendix E, except proprietary chemical results are not presented in order to protect proprietary chemical identities. Exposure estimates are based on a combination of high end (90th percentile)⁷ and average values, as would be used for a high-end exposure estimate. The 90th percentile was used for hours per day of workplace exposure, exposure frequency (days per year), exposure duration in years (90th percentile for occupational and 95th percentile for residential exposures), and the time and frequency of chemical bath and filter replacements, conveyor equipment cleaning and chemical bath sampling (minutes per occurrence and number of occurrences per year) and estimated workplace air concentrations. The average value was used for body weight, concentration of chemical in bath, and the number of baths in a given process. However, because some data,

 $^{^{7}}$ For exposure data from the IPC Workplace Practices Questionnaire, this means that 90 percent of the facilities reported a lower value, and ten percent reported a higher value.

3.3 HUMAN HEALTH AND ECOLOGICAL HAZARDS SUMMARY

This section presents a summary of the human health and ecological hazards data that were used in the risk characterization. This information is summarized from toxicity profiles prepared for non-proprietary chemicals identified as constituents in the baths for the MHC technologies evaluated. Table 3.23 lists these chemicals and identifies the MHC process or processes in which these chemicals are used. The electroless copper process is the predominant method now used in MHC. Section 2.1.4 includes more detailed information on bath constituents and concentrations. Throughout this section, toxicity data for proprietary chemicals are not presented in order to protect proprietary chemical identities.

Table 3.23 Known Use Cluster Chemicals and Associated MHC Processes

Table 3.23 K								I
Chemical List	Electroless Copper	Carbon	Conductive Ink	Conductive Polymer	Graphite	Non- Formaldehyde Electroless Copper	Organic- Palladium	Tin- Palladium
2-Ethoxyethanol	~							
1,3-Benzenediol								~
1H-Pyrrole				~				
2-Butoxyethanol Acetate; Butylcellusolve Acetate			~					
Ammonia					~			
Ammonium Chloride	V							
Benzotriazole	~							
Boric Acid	V							
Carbon Black		~	V					
Copper (I) Chloride; Copper	~		~					~
Copper Sulfate; or Cupric Sulfate	~	~			~	V		~
Diethylene Glycol n-Butyl Ether			~					
Diethylene Glycol Ethyl Ether			~					
Diethylene Glycol Methyl Ether			~					
Dimethylaminoborane	V							
Dimethylformamide	~							
Ethanolamine; Monoethanolamine; 2-Aminoethanol	V	V			V			V
Ethylene Glycol	V	V						
Ethylenediaminetetraacetic Acid (EDTA)	~							
Fluoroboric Acid; Sodium Bifluoride	~							~
Formaldehyde	~							
Formic Acid	V							

⁸ Risk was not characterized for the conductive ink technology but human health and ecological hazards data are presented here.

Chemical List	Electroless Copper	Carbon	Conductive Ink	Conductive Polymer	Graphite	Non- Formaldehyde Electroless Copper	Organic- Palladium	Tin- Palladium
Graphite			>		~			
Hydrochloric Acid	V					~	~	~
Hydrogen Peroxide	V					~		/
Hydroxyacetic Acid	~							
Isophorone			>					
Isopropyl Alcohol; 2-Propanol	~					V		~
Lithium Hydroxide								~
m-Nitrobenzene Sulfonic Acid; Sodium m-Nitrobenzenesulfonate	V							
Magnesium Carbonate	V							
Methanol	~		~					
p-Toluene Sulfonic Acid; Tosic Acid	V							
Palladium	V							~
Palladium Chloride								~
Peroxymonosulfuric Acid; Potassium Peroxymonosulfate	~			V	V			
Phenol-Formaldehyde Copolymer			V					
Phosphoric Acid				V				~
Potassium Bisulfate	V							
Potassium Carbonate		~			~			~
Potassium Cyanide	V							
Potassium Hydroxide	~	~				~		
Potassium Persulfate	V					~		
Potassium Sulfate	V							
Potassium-Sodium Tartrate	V							
Silver			/					
Sodium Bisulfate	V						~	~
Sodium Carbonate	V			/			~	
Sodium Chloride								~
Sodium Chlorite	V					V		
Sodium Cyanide	V							
Sodium Hydroxide	V			/		V		~
Sodium Hypophosphite	V						V	
Sodium Persulfate		~			~		~	~
Sodium Sulfate	~							
Stannous Chloride; Tin (II) Chloride	~					V		~
Sulfuric Acid	V	V		V	~	V		~
Tartaric Acid	~							
Triethanolamine; or 2,2',2" - Nitrilotris Ethanol	V							V

Chemical List	Electroless Copper	Carbon	Conductive Ink	Conductive Polymer	Graphite	Non- Formaldehyde Electroless Copper	Organic- Palladium	Tin- Palladium
Trisodium Citrate 5.5- Hydrate; Sodium Citrate							~	
Vanillin								~
Proprietary Chemicals (no. known for alternative)	12				5		1	5

3.3.1 Carcinogenicity

Table 3.24 summarizes the available information pertaining to carcinogenicity for the MHC chemicals, including classifications describing evidence of chemical carcinogenicity. Due to the large number of chemicals in commerce, including approximately 15,000 non-polymeric chemicals produced in significant amounts (i.e., > 10,000 lbs/year), many chemicals have not yet been tested or assigned carcinogenicity classifications. The classifications referenced in this risk assessment are defined below:

EPA Weight-of-Evidence Classification: In assessing the carcinogenic potential of a chemical, EPA classifies the chemical into one of the following groups, according to the weight-of-evidence from epidemiologic, animal and other supporting data, such as genotoxicity test results:

- Group A: Human Carcinogen (sufficient evidence of carcinogenicity in humans).
- Group B: Probable Human Carcinogen (B1 limited evidence of carcinogenicity in humans; B2 sufficient evidence of carcinogenicity in animals with inadequate or lack of evidence in humans).
- Group C: Possible Human Carcinogen (limited evidence of carcinogenicity in animals and inadequate or lack of human data).
- Group D: Not Classifiable as to Human Carcinogenicity (inadequate or no evidence).
- Group E: Evidence of Non-Carcinogenicity for Humans (no evidence of carcinogenicity in adequate studies).

EPA has proposed a revision of its guidelines that would eliminate the above discrete categories while providing a more descriptive classification.⁹

International Agency for Research on Cancer (IARC) Classification: This is a similar weight-of-evidence method for evaluating potential human carcinogenicity based on human data, animal data, and other supporting data. A summary of the IARC carcinogenicity classification system includes:

⁹ The "Proposed Guidelines for Carcinogen Risk Assessment" (EPA, 1996a) propose use of weight-of-evidence descriptors, such as "Likely" or "Known," "Cannot be determined," and "Not likely," in combination with a hazard narrative, to characterize a chemical's human carcinogenic potential; rather than the classification system described above.

- Group 1: Carcinogenic to humans.
- Group 2A: Probably carcinogenic to humans.
- Group 2B: Possibly carcinogenic to humans.
- Group 3: Not classifiable as to human carcinogenicity.
- Group 4: Probably not carcinogenic to humans.

Both of these classification schemes represent judgements regarding the likelihood of human carcinogenicity. Table 3.24 lists all MHC chemicals which have been classified by EPA or IARC. The National Toxicology Program (NTP) is an additional source used to classify chemicals, but its classifications are based only on animal data from NTP studies.

Table 3.24 Available Carcinogenicity Information

Chemical Name ^a	Cancer Slope Factor (mg/kg-day) ⁻¹	Comments/Classifications
Formaldehyde	0.046 ^b	EPA Group B1 (EPA, 1995b) ^c ; IARC Group 2A (IARC, 1995) ^c
Carbon Black	ND	IARC Group 2B (IARC, 1996) ^d
Dimethylformamide	ND	IARC Group 2B (IARC, 1989) ^d
1,3-Benzenediol	ND	IARC Group 3 (IARC, 1987) ^e
Hydrochloric Acid	ND	IARC Group 3 (HSDB, 1995) ^e
Hydrogen Peroxide	ND	IARC Group 3 (IARC, 1987) ^e
Copper (I) Chloride	ND	EPA Group D (EPA, 1995c) ^f
Copper (II) Chloride	ND	EPA Group D (EPA, 1995c) ^f
Palladium; Palladium Chloride	ND	No classification; rats developed respiratory tumors and leukemia at 5 ppm in water (Schroeder & Mitchener, 1971)
Sodium Sulfate	ND	No classification; "equivocal evidence" of tumorigenicity in mice (RTECS, 1995)
Triethanolamine; or 2,2',2"- Nitrilotris Ethanol	ND	No classification; equivocal carcinogenic evidence in animals (NTP, 1994)
Cyclic Ether ^g	not reported ^h	Possible/probable human carcinogen ⁱ
Alkyl Oxide ^g	not reported ^h	Probable human carcinogeni
Trisodium Acetate Amine B ^j	ND	Possible human carcinogen ⁱ

^a Only those chemicals with available data or classifications are listed.

ND: No Data. A cancer slope factor has not been determined for this chemical.

^b Unit risk units were converted from 1.3 x $10^{-5} \mu g/m^{3-1}$ to slope factor units of $(mg/kg-day)^{-1}$ using $20 m^3/day$ inhalation (breathing) rate and 70 kg body weight.

^c EPA Group B: Probable Human Carcinogen (B1 - limited evidence of carcinogenicity in humans); IARC Group 2A: Possibly carcinogenic to humans.

^d IARC Group 2B: Possibly carcinogenic to humans.

^e IARC Group 3: Not classifiable as to human carcinogenicity.

^f EPA Group D: Not classifiable as to human carcinogenicity (inadequate or no evidence).

^g In graphite and electroless copper technologies.

^h Cancer slope factors are available but not reported in order to protect proprietary chemical identities.

¹ Specific EPA and/or IARC groups not reported in order to protect proprietary chemical identities.

^j In electroless copper technology.

For carcinogenic effects, there is presumably no level of exposure that does not pose a small, but finite, probability of causing a response. This type of mechanism is referred to as "non-threshold." When the available data are sufficient for quantification, EPA develops an estimate of the chemical's carcinogenic potency expressed as a "slope factor." The slope factor (q_1^*) is a measure of an individual's excess risk or increased likelihood of developing cancer if exposed to a chemical (expressed in units of $[mg/kg-day]^{-1}$). More specifically, q_1^* is an approximation of the upper bound of the slope of the dose-response curve using the linearized multistage procedure at low doses. "Unit risk" is an equivalent measure of potency for air or drinking water concentrations and is expressed as the upper bound excess lifetime cancer risk per $\mu g/m^3$ in air, or as risk per $\mu g/L$ in water, for continuous lifetime exposures. (Unit risk is simply a transformation of slope factor into the appropriate scale.) Slope factors and unit risks can be viewed as quantitatively derived judgements of the magnitude of carcinogenic effect. These estimates will continue to be used whether the current EPA weight-of-evidence guidelines are retained or the new proposals are adopted. Their derivation, however, may change for future evaluations.

EPA risk characterization methods require a slope factor or unit risk to quantify the upper bound excess cancer risk from exposure to a known or suspected carcinogen. Therefore, formaldehyde is the only non-proprietary chemical for which cancer risk was characterized (see Section 3.4, Risk Characterization).

3.3.2 Chronic Effects (Other than Carcinogenicity)

Adverse effects other than cancer and gene mutations are generally assumed to have a dose or exposure threshold. Therefore, a different approach is needed to evaluate toxic potency and risk for these "systemic effects." Systemic toxicity means an adverse effect on any organ system following absorption and distribution of a toxicant to a site in the body distant from the toxicant's entry point. A reference dose (RfD) is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure through ingestion to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious noncancer effects during a lifetime (in mg/kg-day). Similarly, a reference concentration (RfC) is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious non-cancer effects during a lifetime (in mg/m³) (Barnes and Dourson, 1988). RfDs and RfCs can also be derived from developmental toxicity studies. However, this was not the case for any of the MHC chemicals evaluated. RfDs and RfCs are derived from EPA peer-reviewed study results (for values appearing in EPA's Integrated Risk Information System [IRIS]), together with uncertainty factors regarding their applicability to human populations. Table 3.25 presents a summary of the available RfC and RfD information obtained from IRIS and EPA's Health Effects Assessment Summary Tables (HEAST). One proprietary chemical, in the tin-palladium alternative, has an RfD available; this is not reported to protect the identity of the proprietary chemical.

Table 3.25 Summary of RfC and RfD Information

Chemical Name a	Inhalation	Comments ^c	Oral/Dermal	Comments ^b	
Chemicai Ivame	RfC (mg/m ³)	(Inhalation)	RfD (mg/kg-day)	(Oral/Dermal)	
2-Butoxyethanol Acetate	0.02	Rat, 13 weeks, hematological and liver effects (EPA, 1995d) ^{c, d}	ND		
2-Ethoxyethanol	0.2	Rabbit, 13 weeks, reduced spleen, testicular weights, and white blood cell counts (EPA, 1996b)	0.4	Gavage, rat and mouse, 103 weeks, reduced body weight, testicular degeneration, and enlargement of adrenal gland (EPA, 1995d)	
Ammonia	0.1	Occupational study, lack of irritation to workers exposed to 9.2 ppm concentration (EPA, 1997)	ND		
Diethylene Glycol Ethyl Ether and Acetate	ND		2	Oral, rat, 3-generation study (chronic reproductive), kidney and bladder damage (EPA, 1995d)	
Diethylene Glycol n-Butyl Ether	0.02	Inhalation, rat, 7 hours (EPA, 1995c,d) ^d	ND		
Dimethylformamide	0.03	Inhalation, human, 5+ years, 54 workers for hepatoxicity effects (EPA, 1996b)	ND		
Ethylene Glycol	ND		2	Oral, rat, 2 years, decreased growth, renal calculi (EPA, 1995c)	
Formaldehyde	ND		0.2	Oral, rat, 2 years, GI tract and histopathological changes (EPA, 1995b)	
Hydrochloric Acid	0.007	Rat, respiratory tract hyperplasia, lifetime exposure (EPA, 1995c)	ND		
Isophorone	ND		0.2	Oral, dog, 90 days, no signs of cellular changes (EPA, 1995d)	
Methanol	ND		0.5	Gavage, rat, 90 days, decreased brain weights (EPA, 1995c)	
Potassium Cyanide	ND		0.05	Oral, rat, 2 years, no treatment effects on weight gain (EPA, 1995c)	
Silver	ND		0.005	Oral, human, 2 - 9.75 years, argyria of skin, eyes, mouth, and throat (EPA, 1996b)	
Sodium Cyanide	ND		0.04	Oral, rat, 2 years (EPA, 1995c)	

Chemical Name a	Inhalation RfC (mg/m³)	Comments ^c (Inhalation)	Oral/Dermal RfD (mg/kg-day)	Comments ^b (Oral/Dermal)
Stannous Chloride	ND		0.62	Rat, 105 weeks (EPA, 1994a) ^e

^a Only those chemicals with available data are listed. Proprietary chemical data are not presented in order to protect proprietary chemical identities.

ND: No data. An RfD or RfC has not been determined for this chemical.

When an RfD or RfC was not available for a chemical, other toxicity values were used, preferably in the form of a no-observed-adverse-effect level (NOAEL) or lowest-observed-adverse-effect level (LOAEL). These toxicity values were obtained from the published scientific literature as well as unpublished data submitted to EPA on chemical toxicity in chronic or subchronic studies. Typically, the lowest NOAEL or LOAEL value from a well-conducted study was used. (If study details were not presented or the study did not appear to be valid, the reported NOAEL/LOAELs were not used.) But unlike the majority of RfD/RfCs, NOAEL/LOAELs have not received EPA peer-review of the studies on which the values are based, and uncertainty factors have not been considered.

The LOAEL is the lowest dose level in a toxicity test at which there are statistically or biologically significant increases in frequency or severity of adverse effects in the exposed population over its appropriate control group (in mg/kg-day, or mg/m³ for inhalation). The NOAEL is the highest dose level in a toxicity test at which there is no statistically or biologically significant increase in the frequency or severity of adverse effects in the exposed population over its appropriate control (in mg/kg-day, or mg/m³ for inhalation). LOAEL values are presented only where NOAELs were not available. Table 3.26 presents a summary of the available NOAEL and LOAEL values.

Table 3.26 NOAEL/LOAEL Values

Chemical Name ^a	Inhalation NOAEL/ LOAEL ^b (mg/m ³)	Comments (Inhalation)	Oral/Dermal NOAEL/ LOAEL ^b (mg/kg-day)	Comments (Oral/Dermal)
1,3-Benzenediol	ND		100 (N) ^c	Gavage, rat/mouse, 2 years (NTP, 1992)
Ammonium Chloride	ND		1,691 (N)	Oral, mouse, developmental study in drinking water (Shepard, 1986)
Benzotriazole	ND		109 (L)	Oral, rat, 26 weeks, induced anemia, endocrine effects (RTECS, 1995)
Boric Acid	ND		62.5 (L)	Gavage, rabbit, developmental study showed cardiovascular defects (U.S. Borax Co., 1992)

^b Comments may include exposure route, test animal, duration of test, effects, and source of data.

^c Based on data for 2-butoxyethanol.

^d Provisional RfC or RfD.

^e Based on data for tin.

Chemical Name ^a	Inhalation NOAEL/ LOAEL ^b (mg/m ³)	Comments (Inhalation)	Oral/Dermal NOAEL/ LOAEL ^b (mg/kg-day)	Comments (Oral/Dermal)
Carbon Black	7.2 (L)	Human, 14 years, decrease in lung function: vital capacity (IARC, 1984)	ND	
Copper (I) Chloride	0.6 (L)	Human, dust caused leukocytosis/anemia, respiratory irritant (U.S. Air Force, 1990)	0.07 (L)	Oral, human, 1.5 years, GI tract effects (ATSDR, 1990a)
Diethylene Glycol Methyl Ether	ND		1,000 (N)	Oral, rat, 13 weeks, kidney damage, (HSDB, 1995)
Diethylene Glycol n-Butyl Ether	NA		191	Dermal, rat, 90 days, hemolytic effects (RM1, 1992)
Dimethylformamide	NA		125 (L)	Oral, rat, 100 days, liver weight increases and body weight gains (Trochimowicz et al., 1994)
Ethanolamine	12.7 (L)	Rat, dog, guinea pig, 90 days, skin irritation/weight loss (ACGIH, 1991)	320 (N)	Oral, rat, 90 days, altered liver/kidney weights at higher concentrations (ACGIH, 1991)
Ethylene Glycol	31	Human, headache, respiratory tract irritation, lymphocytosis (ATSDR, 1993)	NA	
Fluoroboric Acid	ND		0.77	Human, 2 years, bone disease, GI problems & osteoarticular pain in women (HSDB, 1995; based on 50-100 mg/d, for fluorides, adjusted for 65 kg body weight)
Formaldehyde	0.1 ppm (L)	Human, eye and upper respiratory tract irritation (EPA, 1991c) ^d	NA	
Formic Acid	59.2 (N)	Rat/mouse, 2 weeks, respiratory epithelial lesions (Katz and Guest, 1994)	ND	
Graphite	56 (L)	Human effect level for pneumoconiosis, nuisance from dust (Pendergrass, 1983)	ND	

Chemical Name ^a	Inhalation NOAEL/ LOAEL ^b (mg/m³)	Comments (Inhalation)	Oral/Dermal NOAEL/ LOAEL ^b (mg/kg-day)	Comments (Oral/Dermal)
Hydrogen Peroxide	79	Mouse, 7/9 died from 79 mg/m ³ in 6 weeks (EPA, 1988)	630 (N)	Oral, developmental and reproductive studies for 5 weeks (rat) and 3 months (mouse), respectively (IARC, 1985)
Hydroxyacetic Acid	ND		250 (N)	Gavage, developmental rat study showed lung noise, reduced weight gain (DuPont, 1995)
Isopropyl Alcohol, 2-Propanol	980 (N)	Rat, 13 weeks (SIDS, 1995)	100 (N)	Oral, rat, 2-generation study (CMA, 1995; RM2, 1996)
Magnesium Carbonate	Ge	nerally regarded as safe (U	S. FDA as cited	l in HSDB, 1995).
Methanol		Human, 4 year occupational study, vapor caused vision loss (ACGIH, 1991)	NA	
Palladium, Palladium Chloride	ND		0.95 (L)	Oral, rat, 180 days, decreased weight (Schroeder & Mitchener, 1971)
Potassium Hydroxide	7.1	Human, caused cough/bronchial effects, severe eye/skin irritant (Graham et al., 1984)	ND	
Potassium Sodium Tartrate	Ge	nerally regarded as safe (U.	S. FDA as cited	l in HSDB, 1996).
Potassium Sulfate	15 (TC _{LO}) ^e	Rat, 4 hr/d for 17 weeks, metabolic effects (RTECS, 1995)	ND	
Sodium Carbonate	10 (N)	Rat, 4 hr/d, 5 d/w for 3.5 months, decreased weight gain, lung effects (Pierce, 1994)	ND	
Sodium Chlorite	ND		10 (N)	Gavage, rat, 13 weeks, hematological effects (Harrington et al., 1995)
Sodium Hydroxide	2 (L)	Human, dyspnea, irritant (ACGIH, 1991)	ND	
Sodium Sulfate	ND		420 (N)	Oral, rat, 16 weeks (Young, 1992)
Sulfuric Acid	0.066 (N)	Human (EPA, 1994a)	ND	

Chemical Name ^a	Inhalation NOAEL/ LOAEL ^b (mg/m ³)	Comments (Inhalation)	Oral/Dermal NOAEL/ LOAEL ^b (mg/kg-day)	Comments (Oral/Dermal)
Tartaric Acid	ND		8.7	Oral, dog study, 3/4 developed casts (color or tint) in urine, weight changes and advanced renal tubular degeneration, at 990 g/kg for 90-114 days (Informatics, Inc., 1974)
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	ND		32 (L)	Dermal, mouse, 105 weeks, irritation effects (NTP, 1994)
Vanillin	ND		64 (L)	Oral, rat, 10 weeks, growth depression and damage to kidney, myocardium, liver and spleen (Kirwin and Galvin, 1993)

^a Only those chemicals with available data are listed. Proprietary chemical data are not presented in order to protect proprietary chemical identities.

ND: No Data. A NOAEL or LOAEL was not available for this chemical.

NA: Not Applicable. A NOAEL or LOAEL is not required because an RfD or RfD was available for this chemical.

Neither RfDs/RfCs nor LOAELs/NOAELs were available for several chemicals in each MHC process alternative. For these chemicals, no quantitative estimate of risk could be calculated. EPA's Structure-Activity Team (SAT)¹⁰ has reviewed the chemicals without relevant toxicity data to determine if these chemicals are expected to present a toxicity hazard. This review was based on available toxicity data on structural analogues of the chemicals, expert judgement, and known toxicity of certain chemical classes and/or moieties. Chemicals received a concern level rank of high, medium, or low. Results of the SAT evaluation are presented in Table 3.27. A summary of the SAT results for proprietary chemicals is presented in Table 3.28. An overview of chemicals and available toxicity data is presented in Table 3.29.

b When more than one NOAEL and/or LOAEL was available, only the lowest available NOAEL or LOAEL was used and is listed here. If both NOAEL and LOAEL data are available, the NOAEL is used and is listed here.

 $^{^{\}circ}$ (N) = NOAEL; (L) = LOAEL. If neither is indicated, the toxicity measure was not identified as a NOAEL or LOAEL in the available information.

^d This value is highly uncertain; precise thresholds for these irritant effects of formaldehyde have not been established. Estimates based on a large number of clinical and non-clinical observations indicate that most people have irritant reaction thresholds over the range of 0.1 to 3.0 ppm formaldehyde (EPA, 1991c).

^e TC₁₀ = total concentration resulting in a sublethal effect.

¹⁰ The SAT is a group of expert scientists at EPA who evaluate the potential health and environmental hazards of new and existing chemicals.

Table 3.27 Summary of Health Effects Information (from Structure-Activity Team Reports)

Chemical	SAT Health Effects (pertaining to dermal or inhalation exposure)	Overall Concern Level
Dimethylaminoborane	Absorption is expected to be good via all routes of exposure. This compound is corrosive when handled in concentrated form. There is concern for developmental toxicity and reproductive effects for the boron.	High concern
EDTA, Sodium Salt	Expect no absorption by skin, but expect absorption by lungs and GI tract. Compound is a chelator and is expected to chelate Ca and Mg. Concerns for developmental toxicity and cardiac arrhythmia due to ability to chelate Ca. Arrhythmia expected to occur only at high doses.	Low moderate concern
Fluoroboric Acid	Expect absorption via the skin following irritation. Expect good absorption via the lungs and GI tract. This compound is a severe skin irritant and may be corrosive. There is uncertain concern for developmental toxicity based on information for fluoride.	High concern
Graphite	Expect absorption to be nil by all routes. There is concern for lung effects through lung overall (fibrosis) with repeated inhalation exposure of respirable particles.	Low moderate concern
Magnesium Carbonate	Absorption is expected to be nil through the skin and good through the lungs and GI tract. This compound is used as an antacid.	Low moderate concern
m-Nitrobenzene Sulfonic Acid, Sodium Salt	Absorption is expected to be nil through the skin and good through the lungs and GI tract. The nitro group can be reduced to anamine. There is concern for methemoglobinemia as an aromatic amine compound. As a nitrobenzene derivative, there is concern for neutrotoxicity and developmental toxicity. Serious brain damage was noted at 125 ppm in a 2-week inhalation study with nitrobenzene. It is expected to be irritating to mucous membranes and the upper respiratory tract.	Moderate concern
Monopotassium Peroxymonosulfate	Absorption is expected to be nil through the skin and good through the lungs and GI tract. The peroxymonosulfate moiety is reactive with moisture (oxidizing agent). This material will be an irritant as a concentrated solution.	Moderate concern
Palladium Chloride	Absorption is expected to be nil through the skin and good through the lungs and GI tract. It is an irritant and is reported to be a dermal sensitizer in humans (HSDB).	Moderate high concern
Phosphoric Acid	Expect absorption by all routes. Compound is corrosive.	Moderate concern for corrosive effects to all tissues

Chemical	SAT Health Effects (pertaining to dermal or inhalation exposure)	Overall Concern Level
Potassium Bisulfate	Absorption is expected to be nil through the skin as the neat material and good through the lungs and GI tract. Expect absorption via the skin in solution because of damage to the skin. This compound is expected to be a severe irritant and/or corrosive to the skin, eyes, and mucous membranes because of its acidity.	Moderate concern
Potassium Carbonate	Absorption is expected to be nil through the skin and good through the lungs and GI tract. This material is an alkaline solution and is irritating to the skin, mucous membranes, and upper respiratory tract.	Low moderate concern
Potassium Persulfate	Absorption may occur through the skin following irritation of the skin. Absorption is expected to be good via the lungs and GI tract with reaction of the persulfate (oxidizing agent). This compound is irritating and/or corrosive to the skin, eyes, and mucous membranes. It may also be a dermal and respiratory sensitizer.	Moderate concern
Potassium Sulfate	Absorption is expected to be nil through the skin and good through the lungs and GI tract. No significant adverse effects expected.	Low concern
p-Toluene Sulfonic Acid	Expect no absorption by skin, moderate absorption by GI tract, and good absorption by lungs. TSCA Section 8e-10286 report that this chemical is a severe skin irritation. No other health concern identified.	Low moderate concern
Sodium Bisulfate	Absorption is expected to be nil through the skin as the neat material and good through the lungs and GI tract. Expect absorption via the skin in solution because of damage to the skin. This compound is expected to be a severe irritant and/or corrosive to the skin, eyes, and mucous membranes because of its acidity.	Moderate concern
Sodium Hypophosphite	Absorption is expected to be nil through the skin and good through the lungs and GI tract. It is irritating to mucous membranes and may cause dermal sensitization (HSDB).	Low moderate concern
Sodium Persulfate	Absorption may occur through the skin following irritation of the skin. Absorption is expected to be good via the lungs and GI tract with reaction of the persulfate (oxidizing agent). This compound is irritating and/or corrosive to the skin, eyes, and mucous membranes. It may also be a dermal and respiratory sensitizer. In an inhalation sensory irritation study in mice, mortality occurred at 0.77 mg/l and greater (TSCA Section 8e-12867 Report). Sodium peroxysulfate is positive for dermal sensitization in a human patch test (TSCA Section 8e-2767 Report). Ocular opacity was also reported.	Moderate concern

Table 3.28 Summary of EPA Structure-Activity Team Results for Proprietary Chemicals

Technology	No. of Additional	No. of Additional Trade Secret Chemicals With	SAT Human Health Concern Rank (no. of proprietary chemicals)			
	Trade Secret Chemicals ^a	No Human Health Toxicity Data ^b	Low Low-Moderate M		Moderate	
Electroless Copper	9	4	1	2	1	
Graphite	5	3	0	2	1	
Tin-Palladium	5	4	2	1	1	
Organic-Palladium	1	0	0	0	0	

^a New chemical for this process alternative.

Table 3.29 Available Toxicity Data for Non-Proprietary Chemicals

Chemical	Cancer: Slope Factor (SF), Weight-of-Evidence (WOE) Classification	Inhalation: RfC, NOAEL, or LOAEL	Oral/Dermal: RfD, NOAEL, or LOAEL	SAT
2-Ethoxyethanol		RfC	RfD	
1,3-Benzenediol	WOE		NOAEL	
2-Butoxyethanol Acetate; Butylcellusolve Acetate		RfC		
Ammonia		RfC		
Ammonium Chloride			NOAEL	
Benzotriazole			LOAEL	
Boric Acid			LOAEL	
Carbon Black	WOE	LOAEL		
Copper (I) Chloride; Copper	WOE	LOAEL	LOAEL	
Copper Sulfate; or Cupric Sulfate ^a				
Diethylene Glycol n-Butyl Ether		RfC	Other ^b	
Diethylene Glycol Ethyl Ether			RfD	
Diethylene Glycol Methyl Ether			NOAEL	
Dimethylaminoborane				>
Dimethylformamide	WOE	RfC	LOAEL	
Ethanolamine; Monoethanolamine; 2-Aminoethanol		LOAEL	NOAEL	
Ethylene Glycol		Other ^b	RfD	
Ethylenediaminetetraacetic Acid (EDTA)				~
Fluoroboric Acid; Sodium Bifluoride			Other ^b	/
Formaldehyde	SF, WOE	LOAEL	RfD	
Formic Acid		NOAEL		
Graphite		LOAEL		'
Hydrochloric Acid	WOE	RfC		

b The toxicity data required to calculate cancer risk, hazard quotient, and MOE were not available.

Chemical	Cancer: Slope Factor (SF), Weight-of-Evidence (WOE) Classification	Inhalation: RfC, NOAEL, or LOAEL	Oral/Dermal: RfD, NOAEL, or LOAEL	SAT
Hydrogen Peroxide	WOE	Other ^b	NOAEL	
Hydroxyacetic Acid			NOAEL	
Isophorone			RfD	
Isopropyl Alcohol; 2-Propanol		NOAEL	NOAEL	
Lithium Hydroxide				'
m-Nitrobenzene Sulfonic Acid; Sodium m-Nitrobenzenesulfonate				~
Magnesium Carbonate				'
Methanol		Other ^b	RfD	
p-Toluene Sulfonic Acid; Tosic Acid				~
Palladium			LOAEL	
Palladium Chloride			LOAEL	~
Peroxymonosulfuric Acid; Potassium Peroxymonosulfate				~
Phenol-Formaldehyde Copolymer				
Phosphoric Acid				~
Potassium Bisulfate				~
Potassium Carbonate				~
Potassium Cyanide			RfD	
Potassium Hydroxide		Other ^b		
Potassium Persulfate				~
Potassium Sulfate		Other ^b		~
Potassium-Sodium Tartrate ^c				
Silver			RfD	
Sodium Bisulfate				~
Sodium Carbonate		NOAEL		
Sodium Chloride ^d				
Sodium Chlorite			NOAEL	
Sodium Cyanide			RfD	
Sodium Hydroxide		LOAEL		
Sodium Hypophosphite				'
Sodium Persulfate				'
Sodium Sulfate			NOAEL	
Stannous Chloride; Tin (II) Chloride			RfD	
Sulfuric Acid		NOAEL		
Tartaric Acid			Other ^b	

Chemical	Cancer: Slope Factor (SF), Weight-of-Evidence (WOE) Classification	Inhalation: RfC, NOAEL, or LOAEL	Oral/Dermal: RfD, NOAEL, or LOAEL	SAT
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol			LOAEL	
Trisodium Citrate 5.5-Hydrate; Sodium Citrate				~
Vanillin			LOAEL	

^a The toxicity data for copper (I) chloride was used to evaluate copper sulfate and cupric sulfate.

Chemicals having potential developmental toxicity were identified based on the data provided in the toxicity profiles. The data are summarized in Table 3.30. The values listed in the table included the no-observable-effect level (NOEL) or, in the absence of a NOEL, the lowest-observable-effect level (LOEL) concentrations. Chemicals which have inconclusive data concerning the developmental toxicity, as a result of multiple studies having conflicting conclusions, are identified as possible developmental toxicants. The chemical is listed as a possible toxicant given the uncertainty in the data.

^b Toxicity data other than an RfC, RfD, NOAEL, or LOAEL was used. See Table 3.26 for description of the toxicity data.

^c Potassium-sodium tartrate added directly to human food is affirmed as generally regarded as safe when meeting specified food manufacturing requirements (U.S. FDA as cited in HSDB, 1996).

^d Sodium chloride (table salt) is a necessary mineral and electrolyte in humans and animals, and under normal conditions the body efficiently maintains a systemic concentration of 0.9 percent by retaining or excreting dietary sodium chloride. It is not generally considered poisonous to humans or animals, its main systemic effect being blood pressure elevation.

Table 3.30 Developmental Hazards Summary

Chemical Name	Oral NOEL (mg/kg/day) ^a	Comments	Inhalation NOEL (mg/m³)a	Comments
Ammonium Chloride	1,691	Drinking water, mice, after day 7 of gestation. No congenital effects (Shepard, 1986).	NA	
Boric Acid	125	Oral, rabbits, gestation days 6-19. Prenatal mortality, interventricular septal defect, unspecified malformations (U.S. Borax Co., 1992).	NA	
2-Butoxyethanol - possible inhalation	100	Oral, rats, gestation days 9-11 or 11-13. Reduced prenatal viability noted (Gingell et al., 1994).	50 ppm	Rats exposed 6 hours/day on gestation days 6-15 to 100 and 200 ppm. Maternal toxicity noted and increased resorbed litters, decreased pup viability, and delayed ossification (Rohm and Haas, 1992). In another study, rats exposed 7 hours/day to 150 and 200 ppm on gestation days 7-15 had maternal toxicity (transient hemoglobinuria), but no developmental toxicity (Gingell et al., 1994).
Copper	51.7	Food, mice, 30 days before mating through day 19 of gestation. Malformations (EPA, 1984a).	NA	
Diethylene Glycol Methyl Ether	150 (LOEL)	Oral, mice, gestation days 6-15. Malformation of neural tube, heart, renal and skeletal systems (Price et al., 1987).	NA	
2-Ethoxyethanol	93.1	Oral, rats, gestation days 1-21. Increase major skeletal malformations (EPA, 1984b).	369 (LOEL)	Mice, exposure of 6 hours/day, days 6-15 of gestation. Developmental neurotoxicity (EPA, 1996b; 1985a).
Ethanolamine	50 (LOEL)	Oral, rats, gestation days 6-15. Increases in intrauterine deaths, malformations, and increased fetal weight (Mankes, 1986 as reported in TOXLINE, 1995).	NA	

Chemical Name	Oral NOEL (mg/kg/day) ^a	Comments	Inhalation NOEL (mg/m³)a	Comments
Ethylene Glycol	500	Oral, mice, gestation days 6-15. Lower body weights and craniofacial and skeletal malformations (Shell Oil, 1992a).	150	Rats and mice, exposure of 6 hours/day, days 6-15 of gestation. Fetal malformations in mice (exencephaly, cleft palate, and abnormal rib and facial bones) (Shell Oil, 1992b; Union Carbide, 1991).
Ethylenediaminetetraacetic Acid (EDTA)	954 - LOEL	Diet, rats, gestation days 7-14. Maternal-toxicity and reduced litters, reduced fetal weight and malformations (EPA, 1987).	NA	
Hydrazine	NA	Subcutaneous, rats, gestation days 11-21. Injection of 8 mg/kg/day resulted in reduced ratio of fetal survivors to implantation sites, reduced fetal weight, and 100% mortality of pups within 24 hrs of birth (Lee and Aleyassine, 1970).	NA	
Hydrochloric Acid	NA		450 (LOEL)	Rats, exposure of 1 hour/day for 12-16 days prior to mating or on gestation day 9. Adults exhibited mortality. Increased fetal mortality, decreased fetal weight and increased fetal lung weights (EPA, 1995c).
Hydroxylamine Sulfate	NA	Mice. No details given for type of exposure, duration, or dose. Resulted in early fetal deaths and pre-implantation losses (Gross, 1985).	NA	
Isopropanol	480	Oral, rabbits, gestation days 6-18. Reduced fetal body weights noted in oral exposure of rats, but at concentrations with maternal toxicity. No teratogenic effects noted (Tyl, et al., 1995, as cited in CMA, 1995).	3,000 ppm (LOEL)	Rats, exposure of 7 hours/day, gestation days 1-19. Reduced fetal weight (Nelson et al., 1943 as cited in ACGIH, 1991).

Chemical Name	Oral NOEL (mg/kg/day) ^a	Comments	Inhalation NOEL (mg/m³)a	Comments
Isophorone	NA		50 ppm	Rats, exposure of 6 hours/day, gestation days 6-15. Reduction in mean crown-rump length, significant decrease in maternal body weight noted (Bio/Dynamics Inc., 1984).
Lithium Hydroxide	NA	Studies indicate that the risk of major congenital malformations in offspring from women receiving lithium during early pregnancy is slightly higher (4-12%) than that among control groups (2-4%) (Cohen et al., 1994 as cited in Opresko, 1995). Lithium chloride has been shown to cause cleft palate in rats and mice, but lithium carbonate was negative for developmental effects in monkeys, rabbits, and rats (Beliles, 1994). However other studies have shown an increase incidence of cleft palate in mice (Szabo, 1970 as cited in Opresko, 1995).	NA	
Methanol	NA	Drinking water, folate-deficient rats, gestation days 6-15. Maternal toxicity (decreased weight gain) and developmental toxicity (increased resorption) observed at drinking water concentrations of 1% and 2% (Lington and Bevan, 1994).	6,650 (LOEL)	Mice, exposure of 7 hours/day, gestation days 7-9. Increased exencephaly (Lington and Bevan, 1994).
N,N-Dimethylformamide	200	Dermal, rats, gestation days 8-16 (EPA, 1986). Hydrocephalus, growth retardation, post-implantation losses, and increase mortality in offspring (IARC, 1989).	0.05 (LOEL)	Rabbits, exposure of 4 hours/day, days 1-19 of gestation. Reduced fetal growth (IARC, 1989).
Phenol	60	Oral, rats, gestation days 6-15. Reduced fetal body weights (EPA, 1996c).	NA	

Chemical Name	Oral NOEL (mg/kg/day) ^a	Comments	Inhalation NOEL (mg/m³)a	Comments
Potassium Carbonate	NA	Epidemiology study of 226 males employed at potash mine. After starting work underground, mean birth weights increased slightly and there was a decrease in male/female ratio (Wiese and Skipper, 1986).	NA	
Potassium and Sodium Cyanide	NA (276.6 mg CN/kg diet)	Oral, pigs, through gestation and lactation. Fetuses had reduced thyroid, spleen, and heart weights. Sows showed hyperplasia of kidney glomeruli and histological changes in thyroid (Tewe and Maner, 1981).	NA	
Silver - Possible	NA	Silver concentrations in 12 anencephalic human fetuses was higher than silver concentrations in livers of 12 therapeutically aborted fetuses and 14 fetuses aborted spontaneously. Could not be determined if high silver concentrations were associated with the anencephalic malformation or with fetal age (ATSDR, 1990b).	NA	
Sodium Chloride	56,400 (TD _{LO}) ^b	Oral, rats, day 5 or 7 pre-conception and one or more days post-conception. Unspecified toxic effects noted (RTECS, 1996).	NA	
Sodium Chlorite	1.4 (LOEL)	Drinking water, rats, 2.5 months prior to mating through gestational day 20. Increase in variation of sternum and increase in crown-rump length. Same study, oral dose 200 mg/kg/day and 2,800 mg/kg/day via drinking water, gestational days 8-15, no developmental effects (Perry et al., 1994).	NA	

Chemical Name	Oral NOEL (mg/kg/day) ^a	Comments	Inhalation NOEL (mg/m³)a	Comments
Sodium Sulfate	2,800	Oral, mice, gestation days 8-12. No effect on body weights or litter sizes (Young, 1992). Parentally administered dose of 60 mg/kg on day 8 of gestation produced developmental abnormalities of the musculosketal system (RTECS, 1995).		
Stannous Chloride	50	Oral, mice, 10 consecutive days, no effect on gestation of fetal survival (Gitilitz and Moran, 1983). Method of exposure unknown, rats, gestation days 7-12. 500 mg/kg resulted in teratogenic effects (Wu, 1990, as reported in TOXLINE, 1995).		

Unless otherwise noted.
 TD_{Lo} = The lowest dose of a chemical that is expected to cause a defined toxic effect.
 NA: Not applicable. Data for calculating a dose were not available.

3.3.3 Ecological Hazard Summary

Table 3.31 presents a summary of the available ecological hazard information. Concern concentrations (CCs) were determined only for aquatic species (e.g., *Daphnia*, algae, and/or fish) using standard EPA methodology. Methods for determining CCs are summarized below. (*Cleaner Technologies Substitutes Assessment: A Methodology and Resources Guide* [Kincaid et al., 1996] presents the methods in more detail.)

Table 3.31 Aquatic Toxicity Information

Chemical Name ^a		Test	Species	CC	Source	
Chemicai Name	$ ext{LC}_{50} \ (ext{mg/L})^{ ext{b}}$	Information	Species		Source	
1.2 D				(mg/L) ^c	AOLUBE	
1,3-Benzenediol	> 100	all 96 hr	rainbow trout	$AsF = 100^{(2)}$	AQUIRE,	
	0.25		water flea	0.0025	1995	
	88.6		minnow			
	262		zebra fish			
	> 100	40.4	snail	100(2)		
2-Butoxyethanol Acetate	150	48 hr	water flea	$AsF = 100^{(2)}$	Verschueren,	
	960	17 hr	protozoa	1.5	1996	
	> 500	72 hr	green algae			
2-Ethoxyethanol	> 5,000	24 hr	goldfish	$AsF = 1,000^{(3)}$	_	
	> 10,000	96 hr	bluegill &	5.0	1996;	
			silversides		EPA, 1985a	
	7,660	48 hr IC ₅₀ ^d	water flea			
Ammonia	0.42-0.84	8 hr	rainbow trout	$AsF = 100^{(2)}$	AQUIRE,	
	1.74	24 hr	water flea	CC = 0.0042	1995	
	1.58	24 hr	snail			
Ammonium Chloride	640	24 hr TLm ^e	carp	$AsF = 1,000^{(3)}$	Verscheuren,	
	139	24-96 hr TLm	bluegill	0.05	1983	
	50	96 hr TLm	water flea			
Boric Acid	46-75	7 day	goldfish	$AsF = 1,000^{(3)}$	AQUIRE,	
	22-155	9 day	catfish	0.022	1995	
	79-100	28 day	rainbow trout			
Carbon Black		No infor	nation found in literature			
Copper	0.8-1.9	96 hr	carp	$AsF = 100^{(2)}$	AQUIRE,	
	0.0885-21	96 hr	minnow	0.00088	1995	
	0.13-0.5	96 hr	rainbow trout			
	0.125	96 hr	salmon			
	10-33	24 hr	shrimp			
Copper Chloride (Cuprous)	0.40-2.3	96 hr	mummichog	$AsF = 1,000^{(3)}$	AQUIRE,	
			(fish)	0.0004	1995	
Copper Sulfate	0.18-12	96 hr	bullhead	$AsF = 100^{(2)}$	AQUIRE,	
	0.096-0.12	96 hr	zebrafish	0.00002	1995	
	0.036-1.38	96 hr	goldfish			
	0.002-160	96 hr	carp			
	0.10-0.24	96 hr	salmon			
	0.002-23.6	96 hr	minnow			
	0.56-40	96 hr	oyster			
Diethylene Glycol Methyl	> 5,000	24 hr	goldfish	$AsF = 1,000^{(3)}$	AQUIRE,	
Ether	7,500	96 hr	minnow	5.0	1995	
l			1			

Chemical Name ^a	LC_{50}	Test	Species	CC	Source
Chemical I (anic	$(mg/L)^b$	Information	Species	(mg/L) ^c	Bource
Diethylene Glycol	9,650-26,500	96 hr	minnow	$AsF = 100^{(2)}$	AQUIRE,
Ethyl Ether	12,900-13,400	96 hr	rainbow trout	CC = 20	1996
,	15,200	96 hr	mosquito fish		
	6,010	96 hr	catfish		
	1,982-4,670	48 hr	water flea		
Diethylene Glycol	1,300	96 hr	bluegill	$AsF = 100^{(2)}$	AQUIRE,
n-Butyl Ether	3,200	$\mathrm{EC}_{50}^{\mathrm{f}}$	water flea	10	1995
	1,000	decreased cell	blue-green algae	-	
	,	multiplication	8 8		
Dimethylformamide	1.2-2.5	MATC ^g , chronic	water flea	$AsF = 10^{(4)}$	EPA, 1986
	1,300	24 hr	guppy	CC = 0.12	
	> 1,000	48 hr	medaka		
	9,860	96 hr	rainbow trout		
	18,800	48 hr EC ₅₀	water flea		
Ethanolamine	170	96 hr	goldfish	$AsF = 10^{(1)}$	AQUIRE,
	40 & 70	24 hr LC $_0^h$ &	creek chub	CC = 0.075	1995
	140	$\mathrm{LC}_{100}{}^{\mathrm{i}}$	water flea		
	0.75	24 hr	green algae		
		8 day, toxicity			
		threshold			
Ethylene Glycol	41,000	96 hr	rainbow trout	$AsF = 100^{(2)}$	AQUIRE,
	49,000-57,000	96 hr	minnow	CC = 3.3	1995
	41,000-57,600	48 hr	water flea		
	> 5,000	24 hr	goldfish		
	330	48 hr	African frog	(2)	
Ethylenediaminetetraacetic	129	96 hr	catfish	$AsF = 100^{(2)}$	AQUIRE,
Acid (EDTA)	625	24 hr	water flea	CC = 0.41	1995
	59.8	96 hr	minnow		
		96 hr, varying pH			
	280	24 hr	shrimp	1 000(3)	*** 11 . 0
Fluoroboric Acid	125	48 hr	brown trout	$AsF = 1,000^{(3)}$	
	(as fluoride)				Fretwell, 1974
Formaldehyde	25.2-40		bluegill	$AsF = 1,000^{(3)}$	EPA, 1985b
	47.2	96 hr	rainbow trout	CC = 0.0067	
	6.7 25.5-26.3	96 hr 96 hr	striped bass		
E . A . 1			catfish	A E 1 000(3)	AOUIDE
Formic Acid	175	24 hr	bluegill	$AsF = 1,000^{(3)}$	~
	80-90	48 hr	green crab	CC = 0.08	1995
TT 1 11 : A : 1	151	48 hr	water flea	A E 1 000(3)	AOLHDE
Hydrochloric Acid	282	24-96 hr	mosquito fish	$AsF = 1,000^{(3)}$	
	100	96 hr produced no stress effects	green crab	CC = 0.1	1995
	180	96 hr	goldfigh		
Hydro con Dog: 1-			goldfish	A a E 10(1)	AOUDE
Hydrogen Peroxide	89 12	24 hr	mackerel	$AsF = 10^{(1)}$ CC = 1.2	AQUIRE, 1995
	12 155	228 hr LT ₅₀ ^j 24 hr	zebra mussel gobi	CC = 1.2	1773
Isonhoron		24 nr 96 hr	_	A a E 100(2)	AOUDE
Isophorone	12.9 79	96 nr NOEC ^k	mysid shrimp	$AsF = 100^{(2)}$ CC = 0.13	AQUIRE, 1996
	228	96 hr	green algae minnow	CC = 0.13	1770
	220	70 III	IIIIIIIOW		

Chemical Name ^a	LC ₅₀	Test	Species	CC	Source
	(mg/L) ^b	Information		(mg/L) ^c	
Isopropanol	> 1,400	96 hr	mosquito fish		AQUIRE,
	900-1,100	24 hr	creek chub	CC = 9.0	1995
	1,150	96 hr	shrimp		
	1,800	toxicity threshold			
Lithium Hydroxide			oxicity informatio		T
m-Nitrobenzene Sulfonic	8,600	24 &48 hr	water flea	$AsF = 100^{(2)}$	AQUIRE,
Acid	> 500	48 & 96 hr	trout, guppy,	CC = 5	1995;
			bluegill,		Greim et al.,
26.1	20,200	0.61	minnow	A E 100(2)	1994
Methanol	28,200	96 hr	minnow	$AsF = 100^{(2)}$	AQUIRE,
	20,100	96 hr	rainbow trout	CC = 17	1995
	1,700	48 hr	goldfish		
	2.6-3.1% > 10,000	10-14 day EC ₅₀	algae		
Palladium, Palladium		24 hr LC ₅₀	brine shrimp tubificid worm	$AsF = 1,000^{(3)}$	AOUIDE
Chloride	0.237 0.142	24 hr EC ₅₀ 48 hr EC ₅₀	tubilicia worm	$ASF = 1,000^{-3}$ CC = 0.00014	~
	- '		:1-1-1-		
Phenol-Formaldehyde		xicity information			
Copolymer		nsoluble and is not			
Phosphoric Acid	138	TLm	mosquito fish	$AsF = 1,000^{(3)}$ CC = 0.138	HSDB, 1995
D-4: C: 1-	0.052	96 hr	brook trout		EDA 1000
Potassium Cyanide,	0.052 0.057	96 hr 96 hr	rainbow trout	$ASF = 10^{(4)}$ CC = 0.79	EPA, 1980
Sodium Cyanide	0.037	chronic value	brook trout	CC = 0.79	
Detecsione Hydroxide	85	24 hr		$AsF = 1,000^{(3)}$	AOLIDE
Potassium Hydroxide	83 80	48 hr	mosquito fish mosquito fish	ASF = 1,000° $CC = 0.08$	1995
	80	96 hr	_	CC = 0.08	1993
Potassium Persulfate	1,360	48 hr	guppy carp	$AsF = 100^{(2)}$	AQUIRE,
i otassium i eisumate	234	48 hr	rainbow trout	CC = 0.92	1995
	845	48 hr	guppy	CC = 0.72	1773
	92-251	48 hr	water flea		
Potassium-Sodium Tartrate			exicity information	n available.	
Potassium Sulfate	112	all 96 hr	mussel	$AsF = 1,000^{(3)}$	AQUIRE,
	1,180		adult snail		1995
	3,550		bluegill		
	2,380		bleak		
1H-Pyrrole	210	96 hr	minnow	$AsF = 1,000^{(3)}$	AQUIRE,
_	856	72 hr EC ₅₀	protozoan	CC = 0.21	1996
Silver	0.0514	96 hr	rainbow trout	$AsF = 1,000^{(3)}$	AQUIRE,
	0.064	96 hr	bluegill	CC = 0.000036	1996
	0.036	96 hr	minnow		
	58	98 hr	minnow		
Sodium Bisulfate	58-80	24 & 48 hr	mosquito larvae	$AsF = 1,000^{(3)}$	_ ′
	190	immobilized after	water flea	CC = 0.058	1995
		48 hrs			
Sodium Carbonate	300-320	96 hr	bluegill		AQUIRE,
	297	50 hr	guppy	CC = 2.4	1995
	242	5 day	diatom (algae)		
	524	96 hr	water flea		

Chemical Name ^a	LC_{50}	Test	Species	CC	Source
	$(mg/L)^b$	Information	-	(mg/L) ^c	
Sodium Chloride	4,324-13,750	24 hr-10 day	goldfish	$AsF = 100^{(2)}$	AQUIRE,
	17,550-18,100		mosquito fish	CC = 2.8	1996
	23,000-32,000		damsel fly		
	280-1,940	\geq 24 hr	water flea		
	1,500-5,000	24-96 hr	striped bass		
Sodium Chlorite	75	96 hr	minnow	$AsF = 1,000^{(3)}$	
	0.65	96 hr	mysid shrimp	CC = 0.00016	1994; Albright
	0.161	48 hr	water flea		& Wilson,
G II G'	2 220	241		A E 1 000(3)	1992a,b
Sodium Citrate	3,330	24 hr	water flea	$AsF = 1,000^{(3)}$ CC = 3.3	AQUIRE, 1995
Sodium Hydroxide	125	96 hr	mosquito fish	$AsF = 10^{(1)}$	AQUIRE,
Soutum Hydroxide	30	$24 \text{ hr LC}_{40}^{-1}$	pikeperch	CC = 2.5	1995;
	33-100	48 hr	poacher	CC = 2.3	HSDB, 1995
	≥ 25	chronic	guppy		11300, 1773
Sodium Persulfate	1,667	48 hr	carp	$AsF = 1,000^{(3)}$	VOLUBE
Soutum Fersunate	64.6	48 hr	water flea	CC = 0.065	1995
	388	48 hr	rainbow trout	CC = 0.003	1773
	631	48 hr	guppy		
Sodium Sulfate	200-290	96 hr	amphipoda	$AsF = 100^{(2)}$	AQUIRE,
Soutum Sunate	81	96 hr	bass larvae	CC = 0.81	1995
	204	96 hr	water flea	CC = 0.01	1773
	4,380	96 hr	bluegill		
	3,360	32 day	Myriophyllum -		
	3,200	5 2 am	spicatum		
Stannous Chloride ^m	0.6	30 day lethal conc	*	$AsF = 100^{(2)}$	AQUIRE,
	2.1	7 day	goldfish eggs		1995
	0.09	7 day	toad eggs		
	0.4	28 day	rainbow trout		
			eggs		
Sulfuric Acid	80-90	48 hr	poacher	$AsF = 10^{(1)}$	AQUIRE,
	42	96 hr	mosquito fish	CC = 2.0	1995
	42.5	48 hr	prawn		
	20	7 day, no	water flea		
		mortality			
Tartaric Acid	250-320	$\mathrm{LD_0}^{\mathrm{n}}$	paramecium	$AsF = 10^{(1)}$	Verschueren,
	200	LD ₀ longtime	goldfish	CC = 1.0	1983
		hardwater exp.			
	10	LD ₀ longtime			
		softwater exp.			
Tetrasodium EDTA	360	72 hr	protozoa	$AsF = 10^{(1)}$	AQUIRE,
	663	48 hr	cryptomonad	CC = 1.1	1995
	1,033	EC_{50}	water flea		
	11	8 day, decreased	green algae		
		cell			
	1,030-2,070	multiplication	bluegill		
	<u> </u>	96 hr			

Chemical Name ^a	LC_{50}	Test	Species	CC	Source
	(mg/L) ^b	Information		(mg/L) ^c	
Triethanolamine; or 2,2',2"-	> 5,000	24 hr	goldfish	$AsF = 10^{(1)}$	AQUIRE,
Nitrilotris Ethanol	11,800	96 hr	minnow	CC = 0.18	1995
	176-213 mg/kg	$48 \text{ hr, } LD_0$	carp		
	1.8	8 day, decreased	green algae		
		cell			
		multiplication			
Vanillin	112-121	96 hr	minnow	$AsF = 1,000^{(3)}$	AQUIRE,
	57-123	96 hr	minnow	CC = 0.057	1996;
					Verschueren,
					1996

^a Only those chemicals with data are listed. Proprietary chemical data are not presented in order to protect proprietary chemical identities.

The CC for each chemical in water was calculated using the general equation:

CC = acute or chronic toxicity value ÷ AsF

where:

CC = aquatic toxicity concern concentration, the concentration of a chemical in the aquatic environment below which no significant risk to aquatic organisms is expected.

AsF = assessment factor (an uncertainty factor), the adjustment value used in the calculation of a CC that incorporates the uncertainties associated with: 1) toxicity data (e.g., laboratory test versus field test, measured versus estimated data); 2) acute exposures versus chronic exposures; and 3) species sensitivity. This factor is expressed as an order of magnitude or as a power of ten (EPA, 1984c).

b Lethal concentration (LC_{50}) = the concentration of a chemical in water that causes death or complete immobilization in 50 percent of the test organisms at the end of the specified exposure period. LC_{50} values typically represent acute exposure periods, usually 48 or 96 hours but up to 14 days for fish. Units are mg/L unless otherwise noted.

^c Concern concentration (CC) = most sensitive toxicity value (mg/L) ÷ AsF. AsF = Assessment (uncertainty) factor.

^d Concentration that immobilizes 50 percent of the test population.

^e TLm = Median threshold limit value, or tolerance limit median - equivalent to an LC₅₀ value.

 $^{^{\}rm f}$ EC₅₀ = Effective concentration to 50 percent of a test population.

g MATC = Maximum acceptable toxicant concentration. It is generally defined as the geometric mean of the highest concentration tested at which no significant deleterious effect was observed and the lowest concentration tested at which some significant deleterious effect was observed.

 $^{^{\}rm h}$ LC₀ = Estimated maximum concentration that would not result in death of the exposed organisms.

ⁱ LC_{100} = Lethal concentration to 100 percent of a test population.

 $^{^{\}rm j}$ LT₅₀ = Time for 50 percent of the test population to die at a preselected concentration.

^k NOEC = No-observed effect concentration.

¹ LC_{40} = Lethal concentration to 40 percent of a test population.

^m Stannous chloride is expected to rapidly dissociate in water under environmental conditions, followed by formation of tin complexes and precipitation out of the water column. This process would make stannous chloride much less available for toxic effects to aquatic organisms.

ⁿ LD₀ = Estimated maximum dose that would not result in death of the exposed organisms.

⁽¹⁾ Chronic data available and was most sensitive endpoint, AsF = 10.

 $^{^{(2)}}$ Acute data available for multiple species and trophic levels, AsF = 100.

⁽³⁾ Limited acute data available, AsF = 1,000.

⁽⁴⁾ AsF of 10 used for MATC data.

If several acute or chronic toxicity values are available, the lowest one is used (most sensitive tested species), unless poor or uncertain data quality disqualifies one or more of the values. The AQUIRE database, an extensive source of aquatic toxicity data, includes a numerical rating of study quality.

AsFs are dependent on the amount and type of toxicity data contained in a toxicity profile and reflect the amount of uncertainty about the potential effects associated with a toxicity value. In general, the more complete the toxicity profile and the greater the quality of the toxicity data, the smaller the AsF used.

The following approach was used, depending on availability and type of data:

- If the toxicity profile only contained one or two acute toxicity values (no chronic values), AsF = 1,000 and the CC was calculated by using the lower acute value.
- If the toxicity profile contained three or more acute values (no chronic values), AsF = 100 and the CC was calculated by using the lowest acute value.
- If the toxicity profile contained at least one chronic value, and the value was for the most sensitive species, AsF = 10 and the CC was calculated by using the lowest chronic value. Otherwise, AsF = 100 and the CC was calculated with the acute value for the most sensitive species.
- If the toxicity profile contained field toxicity data, AsF = 1 and CC was calculated by using the lowest value.

Aquatic toxicity values were estimated using the ECOSAR program (EPA, 1994b) for chemicals without available measured acute or chronic aquatic toxicity data. These values are presented in Table 3.32. An AsF of 1,000 was used to calculate all CCs based on such estimates.

Table 3.33 presents chemicals with aquatic toxicity CCs. The chemicals are listed in ascending order (i.e., the chemical with the lowest CC to the chemical with the highest CC for each of the alternatives). The lowest CC is for copper sulfate, based on fish toxicity data. The table also presents aquatic hazard concern levels; chemicals were assigned to aquatic toxicity concern levels according to the following EPA criteria:

For chronic values:

```
\leq 0.1 mg/L.....High concern > 0.1 to \leq 10 mg/L....Moderate concern > 10 mg/L.....Low concern
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For acute values:

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\leq 1 mg/L......High concern > 1 to \leq 100 mg/L.....Moderate concern > 100 mg/L.....Low concern
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Chronic toxicity ranking takes precedence over the acute ranking.

It should be noted that aquatic hazard concern levels are derived from the lowest toxicity value available. Therefore, these rankings are derived separately from the CCs which are derived based on the amount of toxicity data available for a given chemical. A summary of the aquatic toxicity results for the known proprietary chemicals is presented in Table 3.34.

These rankings are based only on chemical toxicity to aquatic organisms, and are not an expression of risk. The number of chemicals with a high aquatic hazard concern level include two in carbon, two in conductive ink, none in the conductive polymer process, nine in the electroless copper process, three in graphite, three in non-formaldehyde electroless copper, two in organic-palladium, and nine in tin-palladium.

Table 3.32 Estimated Ecological (Aquatic)Toxicity Information for Non-Proprietary Chemicals

Chemical	Acute Toxicity (mg/L)			(AsF, CC		
	Fish (FW) 96 hr LC ₅₀	Daphnid 48 hr LC ₅₀	Green Algae 96 hr EC ₅₀	Fish 14 day LC ₅₀	Daphnid 16 day EC ₅₀	Green Algae >96 hr ChV	(mg/L)
Benzotriazole ⁽¹⁾	45.3	378.1	23.4	ND	ND	ND	1,000 0.023
Dimethylaminoborane ⁽²⁾	10	0.7	3.0	1.0	0.070	0.3	10 0.007
Graphite ⁽²⁾	*	*	*	*	*	*	
Hydroxyacetic Acid ⁽¹⁾	> 1,000 *	> 1,000 *	> 1,000 *	ND	ND	ND	1,000 1
Magnesium Carbonate ⁽²⁾	> 100	140	> 100	> 10	82	> 10	10 > 1.0
Peroxymonosulfuric Acid ⁽²⁾	≤ 3.0	≤ 3.0	≤ 3.0	≤ 0.30	≤ 0.30	<u>≤</u> 1.0	10 0.030
Potassium Bisulfate ⁽²⁾	> 1,000	> 100	> 100	> 100	> 10	> 10	10 > 1.0
Potassium Carbonate ⁽²⁾	1,300	330	100	100	190	> 30	10 > 3.0
p-Toluene Sulfonic Acid ⁽²⁾	Predicted toxicity values of environmental base set all > 100 mg/L, chronic values all > 10.0 mg/L based on SARs for anionic LAS surfactants.						10 1.0
Sodium Hypophosphite ⁽²⁾	> 100	> 100	0.030	> 10	> 10	0.060	10 0.006

⁽¹⁾ ECOSAR Program.

ND: No Data. ECOSAR (EPA, 1994b) did not include an estimating component for this endpoint for the chemical class.

⁽²⁾ SAT Report.

^{*} No adverse effects expected in a saturated solution.

Table 3.33 Aquatic Hazard Concern Concentrations (CCs) and Hazard Concern Levels by MHC Technology for Non-Proprietary Chemicals

by MHC Technology in Chemicals in MHC Processes	CCs	Aquatic Hazard Concern
	(mg/L)	Level ^b
Electroless Copper		
Copper Sulfate	$0.00002^{(2)}$	High ^(A)
Palladium; Palladium Chloride	$0.00014^{(3)}$	High ^(A)
Sodium Chlorite	$0.00016^{(3)}$	High ^(A)
Copper Chloride	$0.0004^{(3)}$	High ^(A)
Stannous Chloride ^c	$0.0009^{(2)}$	High ^(A)
Sodium Hypophosphite	$0.006^{(5)}$	Low ^(A)
Formaldehyde	$0.0067^{(3)}$	Moderate ^(A)
Dimethylaminoborane	$0.007^{(5)}$	High ^(C)
Boric Acid	0.022(3)	Moderate ^(A)
Benzotriazole	0.023(5)	Moderate ^(A)
Peroxymonosulfuric Acid	0.030 ⁽⁵⁾	Moderate ^(C)
Ammonium Chloride	$0.05^{(3)}$	Moderate ^(A)
Sodium Bisulfate	$0.058^{(3)}$	Moderate ^(A)
Ethanolamine	0.075(1)	High ^(A)
Potassium Hydroxide	$0.08^{(3)}$	Moderate ^(A)
Formic Acid	$0.08^{(3)}$	Moderate ^(A)
Potassium Hydroxide	$0.08^{(3)}$	Moderate ^(A)
Hydrochloric Acid	$0.1^{(3)}$	Moderate ^(A)
Potassium Sulfate	0.11(3)	Low ^(A)
Dimethylformamide	$0.12^{(4)}$	Moderate ^(C)
Fluoroboric Acid	0.125(3)	Low ^(A)
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	0.18(1)	Moderate ^(C)
Ethylenediaminetetraacetic Acid (EDTA)	0.41(2)	Moderate ^(A)
Sodium Cyanide	$0.79^{(1)}$	High ^(C)
Potassium Cyanide	$0.79^{(1)}$	High ^(C)
Sodium Sulfate	$0.81^{(2)}$	Moderate ^(A)
Potassium Persulfate	$0.92^{(2)}$	Moderate ^(A)
Hydroxyacetic Acid	1 ⁽⁵⁾	Low ^(A)
Magnesium Carbonate	$1.0^{(5)}$	Low ^(C)
p-Toluene Sulfonic Acid	1.0 ⁽⁵⁾	Low ^(C)
Tartaric Acid	1.0(1)	Moderate ^(C)
Potassium Bisulfate	>1.0(5)	Low ^(C)
Hydrogen Peroxide	1.2(1)	Low ^(C)
Sulfuric Acid	2.0(1)	Low ^(C)

Chemicals in MHC Processes ^a	CCs (mg/L)	Aquatic Hazard Concern Level ^b		
Sodium Carbonate	2.4 ⁽²⁾	Low ^(A)		
Sodium Hydroxide	2.5(1)	Low ^(C)		
Ethylene Glycol	3.3 ⁽²⁾	Low ^(A)		
m-Nitrobenzene Sulfonic Acid	5 ⁽²⁾	Low ^(A)		
2-Ethoxyethanol	5.0(3)	Low ^(A)		
Isopropanol	9.0(2)	Low ^(A)		
Methanol	17 ⁽²⁾	Low ^(A)		
Potassium-Sodium Tartrate	no data	a available		
Carbon				
Copper Sulfate	$0.00002^{(2)}$	High ^(A)		
Sodium Persulfate	$0.065^{(3)}$	Moderate ^(A)		
Ethanolamine	$0.075^{(1)}$	High ^(A)		
Potassium Hydroxide	$0.08^{(3)}$	Moderate ^(A)		
Sulfuric Acid	$2.0^{(1)}$	Low ^(C)		
Potassium Carbonate	> 3.0 ⁽⁵⁾	Low ^(C)		
Ethylene Glycol	3.3(2)	Low ^(A)		
Carbon Black	no data available			
Conductive Ink				
Silver	$0.000036^{(3)}$	High ^(A)		
Copper	$0.00088^{(2)}$	High ^(A)		
Isophorone	$0.13^{(2)}$	Moderate ^(A)		
2-Butoxyethanol Acetate	1.5 ⁽²⁾	Low ^(A)		
Diethylene Glycol Methyl Ether	5.0(3)	Low ^(A)		
Diethylene Glycol n-Butyl Ether	$10^{(2)}$	$Low^{(A)}$		
Methanol	17 ⁽²⁾	$Low^{(A)}$		
Diethylene Glycol Ethyl Ether	$20^{(2)}$	$Low^{(A)}$		
Graphite	not expected to be toxic ⁽⁵⁾	Low		
Phenol-Formaldehyde Copolymer	not expected to be toxic ⁽⁵⁾	Low		
Carbon Black	no data available			
Conductive Polymer				
Peroxymonosulfuric Acid	$0.030^{(5)}$	Moderate ^(C)		
Phosphoric Acid	0.138 ⁽³⁾	Low ^(A)		
1H-Pyrrole	0.21(3)	Low ^(A)		
Sulfuric Acid	$2.0^{(1)}$	Low ^(C)		
Sodium Carbonate	2.4 ⁽²⁾	Low ^(A)		
Sodium Hydroxide	$2.5^{(1)}$	Low ^(C)		

Chemicals in MHC Processes ^a	CCs (mg/L)	Aquatic Hazard Concern Level ^b		
Graphite				
Copper Sulfate	$0.00002^{(2)}$	High ^(A)		
Ammonia	0.0042(2)	High ^(A)		
Peroxymonosulfuric Acid	0.030 ⁽⁵⁾	Moderate ^(C)		
Sodium Persulfate	$0.065^{(3)}$	Moderate ^(A)		
Ethanolamine	$0.075^{(1)}$	High ^(A)		
Sulfuric Acid	2.0(1)	Low ^(C)		
Potassium Carbonate	> 3.0 ⁽⁵⁾	Low ^(C)		
Graphite	not expected to be toxic ⁽⁵⁾	Low		
Non-Formaldehyde Electroless Copper				
Copper Sulfate	$0.00002^{(2)}$	High ^(A)		
Sodium Chlorite	$0.00016^{(3)}$	High ^(A)		
Stannous Chloride ^c	$0.0009^{(2)}$	High ^(A)		
Potassium Hydroxide	$0.08^{(3)}$	Moderate ^(A)		
Hydrochloric Acid	0.1(3)	Moderate ^(A)		
Potassium Persulfate	0.92(2)	Moderate ^(A)		
Hydrogen Peroxide	1.2(1)	Low ^(C)		
Sulfuric Acid	2.0(1)	Low ^(C)		
Sodium Hydroxide	2.5 ⁽¹⁾	Low ^(C)		
Isopropanol	9.0 ⁽²⁾	Low ^(A)		
Organic-Palladium				
Sodium Hypophosphite	$0.006^{(5)}$	High ^(C)		
Sodium Bisulfate	$0.058^{(3)}$	Moderate ^(A)		
Sodium Persulfate	$0.065^{(3)}$	Moderate ^(A)		
Hydrochloric Acid	0.1(3)	Moderate ^(A)		
Sodium Carbonate, Sodium Bicarbonate	2.4 ⁽²⁾	Low ^(A)		
Sodium Citrate	3.3(3)	Low ^(A)		
Tin-Palladium				
Copper Sulfate	$0.00002^{(2)}$	High ^(A)		
Palladium Chloride, Palladium	0.00014(3)	High ^(A)		
Copper	0.00088(2)	High ^(A)		
Stannous Chloride ^c	$0.0009^{(2)}$	High ^(A)		
1,3-Benzenediol	$0.0025^{(2)}$	High ^(A)		
Dimethylaminoborane	0.007 ⁽⁵⁾	High ^(C)		
Vanillin	0.057 ⁽³⁾	Moderate ^(A)		
Sodium Bisulfate	$0.058^{(3)}$	Moderate ^(A)		
Sodium Persulfate	$0.065^{(3)}$	Moderate ^(A)		

Chemicals in MHC Processes ^a	CCs (mg/L)	Aquatic Hazard Concern Level ^b		
Ethanolamine	$0.075^{(1)}$	High ^(A)		
Hydrochloric Acid	$0.1^{(3)}$	Moderate ^(A)		
Fluoroboric Acid	$0.125^{(3)}$	Low ^(A)		
Phosphoric Acid	0.14 ⁽³⁾	Low ^(A)		
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	0.18(1)	Moderate ^(C)		
Hydrogen Peroxide	1.2 ⁽¹⁾	Low ^(C)		
Sulfuric Acid	2.0 ⁽¹⁾ Low ^(C)			
Sodium Hydroxide	2.5 ⁽¹⁾ Low ^(C)			
Sodium Chloride	$2.8^{(2)}$	Low ^(A)		
Potassium Carbonate	> 3.0 ⁽⁵⁾	Low ^(C)		
Isopropanol	9.0 ⁽²⁾ Low ^(A)			
Lithium Hydroxide	no data available			

^a Different supplier's product lines do not necessarily include all of the chemicals listed for a process alternative.

Basis of Concern Concentrations:

Table 3.34 Summary of Aquatic Toxicity for Proprietary Chemicals

Technology	No. of Additional Trade Secret	Aquatic Toxicity Concern Rank		CC (mg/l)				
	Chemicals ^a	Low	Moderate	High	< 0.1	0.9 - 0.99	1 - 10	> 10
Electroless Copper	9	6	3	0	1	2	5	1
Graphite	5	4	1	0	0	2	2	1
Tin-Palladium	5	2	1	2	2	1	1	1
Organic-Palladium	1	0	0	1	1	0	0	0

^a Includes chemicals not previously identified in the publicly-available bath chemistry data for a technology.

3.3.4 Summary

For human health hazards, toxicity data in the form of RfDs, RfCs, NOAELs, LOAELs, and cancer slope (cancer potency) factors were compiled for inhalation and dermal pathways. Formaldehyde was the only non-proprietary chemical with an established cancer slope (cancer potency) factor. Other non-proprietary chemicals in the MHC processes are suspected

^b Based on lowest available toxicity data:

⁽A) indicates the lowest acute value was used for hazard ranking.

⁽C) indicates the hazard ranking is based on a chronic value, if available and lower than any acute value.

^c Stannous chloride is expected to rapidly dissociate in water under environmental conditions, followed by tin forming complexes and precipitating out of the water column. This process would make stannous chloride much less available for toxic effects to aquatic organisms.

⁽¹⁾ Chronic data.

⁽²⁾ Acute data for multiple species and taxonomic groups.

⁽³⁾ Limited acute data.

⁽⁴⁾ Chronic MATC.

⁽⁵⁾ Structure-activity relationship estimate using the ECOSAR program or SAT report.

carcinogens, but do not have established slope factors. Dimethylformamide and carbon black have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Dimethylformamide is used by at least one supplier in the electroless copper process. Carbon black is used in the carbon and conductive ink processes. Two proprietary chemicals used in the graphite and electroless copper processes, cyclic ether and alkyl oxide, have cancer slope factors. Another proprietary chemical used in the electroless copper process, trisodium acetate amine B, is possibly carcinogenic to humans but does not have an established slope factor.

An ecological hazards assessment was performed based on chemical toxicity to aquatic organisms. Concern concentrations (CCs) were estimated for MHC chemicals using an established EPA method. A CC is an acute or chronic toxicity value divided by an assessment factor (AsF). AsFs are dependent on the amount and type of toxicity data contained in a toxicity profile and reflect the amount of uncertainty about the potential effects associated with a toxicity value. Concern concentrations were determined for aquatic species (e.g., *Daphnia*, algae, and/or fish). The lowest CC is for copper sulfate, based on fish toxicity data.

Chemicals were also ranked for aquatic toxicity concern levels using established EPA criteria (high, moderate, and low concern) based on the available toxicity data. The number of chemicals with a high aquatic hazard concern level include nine in the electroless copper process, two in carbon, two in conductive ink, none in conductive polymer, three in graphite, three in nonformaldehyde electroless copper, and nine in the tin-palladium process, and two in the organic palladium process.

3.4 RISK CHARACTERIZATION

Risk characterization is the summarizing step of a risk assessment, which integrates the hazard and exposure assessment components and presents overall conclusions. Risk characterization typically includes a description of the assumptions, scientific judgments, and uncertainties that are part of this process. There are several types of risk assessment ranging from screening level to comprehensive, and differing according to framework: site-specific, single chemical, or multiple chemical. This risk assessment is best described as a screening level assessment of multiple chemicals identified as belonging to a particular use cluster (MHC) in the PWB industry. This is a screening level, rather than a comprehensive risk characterization, both because of the predefined scope of the assessment and because of exposure and hazard data limitations. The intended audience of this risk characterization is the PWB industry and others with a stake in the practices of this industry.

The focus of this risk characterization is on chronic (long-term) exposure to chemicals that may cause cancer or other toxic effects rather than on acute toxicity from brief exposures to chemicals. The focus is also on those health effects from chronic exposures that could be used to measure risk. In addition, this risk characterization does not consider chemical persistence. The Process Safety Assessment (Section 3.5) includes further information on chemical safety concerns.

The goals of the PWB project risk characterization are:

- To present conclusions and uncertainties associated with a screening level health risk assessment of chemicals used in the MHC process of PWB manufacture.
- To integrate chemical hazard and exposure information to assess risks from ambient environment and occupational exposures from the MHC process.
- To use reasonable and consistent assumptions across alternatives, so health risks associated with one alternative can be compared to the health risks associated with other alternatives.
- To identify the areas of concern that differ among the substitutes in a manner that facilitates decision-making.

This section contains a summary of the exposure assessment (Section 3.4.1), the human health hazards assessment (Section 3.4.2), a description of methods used to calculate risk indicators (Section 3.4.3), results (Section 3.4.4), discussion of uncertainties (Section 3.4.5), and conclusions (Section 3.4.6). Detailed exposure data are presented separately in the Exposure Assessment (Section 3.2) and in Appendix E.

3.4.1 Summary of Exposure Assessment

The exposure assessment uses a "model facility" approach, where as much as possible, reasonable and consistent assumptions are used across alternatives. Data to characterize the model facility and exposure patterns for each process alternative were aggregated from a number of sources, including PWB shops in the U.S. and abroad, supplier data, and input from PWB manufacturers at project meetings. Thus, the model facility is not entirely representative of any

one facility, and actual exposure (and risk) could vary substantially, depending on site-specific operating conditions and other factors.

Chemical exposures to PWB workers and the general population were estimated by combining information gathered from industry (IPC Workplace Practices Questionnaire and Performance Demonstration data, MSDSs, and other available information) with standard EPA exposure assumptions (e.g., for inhalation rate, surface area of dermal contact, and other parameters). The pathways identified for potential exposure from MHC process baths were inhalation and dermal contact for workers, and inhalation contact only for the general populace living near a PWB facility.

The possible impacts from chemical spills are not addressed due to the pre-defined scope of this assessment. In addition, environmental releases to surface water were not quantified because chemical constituents and concentrations in wastewater could not be adequately characterized for the MHC line alone. This is because PWB manufacturers typically combine wastewater effluent from the MHC process line with effluent from other PWB manufacturing processes prior to on-site wastewater pretreatment. The pretreated wastewater is then discharged to a POTW. Many PWB manufacturers measure copper concentrations in effluent from on-site pretreatment facilities in accordance with POTW discharge permits, but they do not measure copper concentrations in MHC line effluent prior to pretreatment. Because there are many sources of copper-contaminated wastewater in PWB manufacturing, the contribution of the MHC line to overall copper discharges could not be estimated. Furthermore, most of the MHC alternatives contain copper, but because these technologies are only now being implemented in the U.S., their influence on total copper discharges from a PWB facility cannot be determined. Finally, while data are available on copper discharges from PWB facilities, data are not available for some of the other metals found in alternatives to electroless copper. Although ecological hazards are assessed in Section 3.3, without exposure or release data a comparative evaluation of ecological (aquatic) risk could not be performed.

Inhalation exposure could occur by breathing air containing vapor or aerosol-phase chemicals from the MHC process line. Inhalation exposures to workers from non-conveyorized lines are estimated in the exposure assessment. Inhalation exposure to workers from conveyorized MHC lines is assumed to be negligible because the lines are typically enclosed and vented to the outside. The model used to estimate daily inhalation exposure is from the EPA *Chemical Engineering Branch Manual for the Preparation of Engineering Assessments* (EPA, 1991a):

```
I = (Cm)(b)(h)
```

where:

I = daily inhalation potential dose rate (mg/day) Cm = airborne concentration of substance (mg/m³)

b = inhalation rate (m³/hr) h = duration (hr/day) Daily exposures are then averaged over a lifetime (70 years) for carcinogens, and over the exposure duration (e.g., 25 years working in a facility) for non-carcinogens, 11 using the following equations:

For carcinogens:

```
LADD = (I)(EF)(ED)/[(BW)(AT_{CAR})]
```

For non-carcinogens:

```
ADD = (I)(EF)(ED)/[(BW)(AT_{NC})]
```

where:

LADD = lifetime average daily dose (mg/kg-day)

ADD = average daily dose (mg/kg-day) EF = exposure frequency (days/year)

ED = exposure duration (years)

BW = body weight (kg)

 AT_{CAR} = averaging time for carcinogenic effects (days)

 AT_{NC} = averaging time for non-carcinogenic chronic effects (days)

The daily intake for inhalation exposure to workers was calculated by first modeling chemical emissions from MHC baths with three air-transport mechanisms: liquid surface diffusion (desorption), bubble desorption, and aerosol generation and ejection. This chemical emission rate was combined with data from the IPC Workplace Practices Questionnaire and Performance Demonstration regarding process room size and air turnover rate to estimate an average indoor air concentration for the process area. An uncertainty and sensitivity analysis of the air transport models suggests that the air turnover (ventilation) rate assumption greatly influences the estimated air concentration in the process area because of its large variability (see the Exposure Assessment, Section 3.2.3).

Inhalation exposure to a hypothetical population located near a model PWB facility was estimated using the Industrial Source Complex - Long Term (ISCLT) air dispersion model. The modeled air concentrations of each contaminant were determined at 100 meters radially from a PWB facility, and the highest estimated air concentration was used. This model estimates air concentrations from the process bath emission rates for all processes. These emissions were assumed to be vented to the ambient environment at the rate emitted from the baths. Inhalation exposures estimated for the public living 100 meters away from a PWB facility were very low (approximately 10,000 times lower than occupational exposures).

Different averaging times are used for characterizing risk for carcinogenic and non-carcinogenic effects. For carcinogenic agents, because even a single incidence of exposure is assumed to have the potential to cause cancer throughout an individual's lifetime, the length of exposure to that agent is averaged over a lifetime. An additional factor is that the cancer latency period may extend beyond the period of working years before it is discernible. For chemicals exhibiting non-cancer health effects from chronic (longer-term) exposure, where there is an exposure threshold (a level below which effects are not expected to occur), only the time period when exposure is occurring is assumed to be relevant and is used as the averaging time.

Dermal exposure could occur when skin comes in contact with the bath solution while dipping boards, adding bath replacement chemicals, etc. Although the data suggest that most MHC line operators do wear gloves, it was assumed in this evaluation that workers do not wear gloves to account for the fraction that do not. Otherwise, dermal exposure is expected to be negligible. For dermal exposures, the flux of a material through the skin was estimated based on EPA. 1992a:

D = (S)(C)(f)(h)(0.001)

where:

D = dermal potential dose rate (mg/day)

S = surface area of contact (cm²)

C = concentration of chemical in the bath (mg/L)

f = flux through skin (cm/hour)

h = duration (hours/day)

with a conversion factor of 0.001 (L/cm³)

It should be noted that the above equation was developed for exposures with an infinite volume of liquid or boundary layer contacting the skin, such as swimming or bathing. Occupational conditions of dermal contact are likely to be more finite in comparison, resulting in possible overestimates of flux through the skin.

As for inhalation, daily dermal exposures were then averaged over a lifetime for carcinogens, and over the exposure duration for non-carcinogens, using the following equations:

For carcinogens:

$$LADD = (D)(EF)(ED)/[(BW)(AT_{CAR})]$$

For non-carcinogens:

$$ADD = (D)(EF)(ED)/[(BW)(AT_{NC})]$$

For dermal exposure, the concentration of chemical in the bath and duration of contact for workers was obtained from publicly-available bath chemistry data, disclosed proprietary chemical information, and IPC Workplace Practices Questionnaire information, respectively. A permeability coefficient (rate of penetration through skin) was estimated for organics and a default rate assumption was used for inorganics. Reliance on such estimates in the absence of data is a source of uncertainty in the exposure assessment.

Key assumptions in the exposure assessment include the following:

- For dermal exposure, it was assumed that line operators do not wear gloves. Although the data suggests that most MHC line operators do wear gloves, it was assumed for this evaluation that workers do not wear gloves to account for the subset of workers who do not wear proper personal protective equipment.
- For dermal exposure, it was assumed that all non-conveyorized lines are manual hoist.

- The worker is assumed to have potential dermal contact for the entire time spent in the MHC area, divided equally among the baths. This does not mean that a worker has both hands immersed in a bath for that entire time; but that the skin is in contact with bath solution (i.e., the hands may remain wet from contact). This assumption may result in an overestimate of dermal exposure.
- For estimating ambient (outdoor) air concentrations, it was assumed that no air pollution control technologies are used to remove airborne chemicals from facility air prior to venting it to the outside.
- For inhalation exposure to workers, it was assumed that chemical emissions to air in the process room from conveyorized lines are negligible, and that no vapor control devices (e.g., bath covers) are used on baths in non-conveyorized lines.
- For air concentrations, the model assumes complete mixing in the process room and that concentrations do not change with time (steady state).
- For all exposures, it was assumed that there is one MHC process line and one line operator per shift in a process area.
- For characterizing the chemical constituents in the MHC process baths, it was assumed that the form (speciation) and concentration of all chemicals in the baths are constant over time, and that MSDSs accurately reflect the concentrations in product lines. If reported constituent weight percents on an MSDS total less than 100 percent, the remainder is assumed to be water. These assumptions are discussed further below.

The exposure assessment does not account for any side reactions occurring in the baths (e.g., the Cannizarro side reaction, which involves the reaction of formaldehyde in electroless copper baths). A study performed by Merix Corporation found that for every one mole of formaldehyde reacting in the intended copper deposition process, approximately one mole was reacting with hydroxide in a Cannizarro side reaction to produce formate ion and methanol (Williamson, 1996). Other studies have found that the Cannizarro reaction tendency increases with the alkalinity of the bath. The exposure assessment assumed that the formaldehyde in the bath is not reacted, and is available to be emitted as formaldehyde. This assumption could tend to overestimate formaldehyde exposures, and thus risk. However, if side reactions are occurring with other chemicals that result in the formation of other toxic chemicals (such as methanol), risk from these chemicals could be underestimated. A search for literature references to studies of side reactions occurring in PWB baths did not produce sufficient information to quantify the risk of reaction products in this risk characterization.

Chemical concentrations in baths are based on publicly-available chemistry data, including MSDSs, partial proprietary chemical information, and supplier Product Data Sheets that describe how to mix and maintain chemical baths. Many MSDSs provided concentration ranges for chemical constituents instead of absolute concentrations, in which case it was assumed that a chemical is present at the mid-point of the reported concentration range. This assumption may either overestimate or underestimate risk for chemicals, depending on their actual concentrations.

Using MSDS data for an exposure assessment can also lead to an underestimate of overall risk from using a process because the identities of many proprietary ingredients are not included

in the MSDSs. Efforts were made to obtain this information from suppliers of MHC bath formulations and proprietary information has been received from three of the seven suppliers.¹²

Assumptions and parameter values used in these equations and results of the exposure calculations are presented in the Exposure Assessment (Section 3.2). In order to provide information about the position an exposure estimate has in the distribution of possible outcomes, exposure (or risk) descriptors are used following EPA's (EPA, 1992b) *Guidelines for Exposure Assessment*. For this risk characterization, the exposure assessment uses whenever possible a combination of central tendency (either an average or median estimate) and high-end (90th percentile)¹³ assumptions, as would be used for an overall high-end exposure estimate. The 90th percentile is used for:

- Hours per day of workplace exposure.
- Exposure frequency (days per year).
- Exposure duration in years (90th percentile for occupational and 95th percentile for residential exposures).
- The time and frequency of chemical bath and filter replacements, conveyor equipment cleaning and chemical bath sampling (minutes per occurrence and number of occurrences per year).
- Estimated workplace air concentrations.

Average values are used for:

- Body weight.
- Concentration of chemical in bath.
- The number of baths in a given process.

Some values used in the exposure calculations, however, are better characterized as "what-if," especially pertaining to bath concentrations, use of gloves, and process area ventilation rates for the model facility. ("What-if" represents an exposure estimate based on postulated questions, making assumptions based on limited data where the distribution is unknown.) Because some part of the exposure assessment for both inhalation and dermal exposures qualifies as a "what-if" descriptor, the entire assessment should be considered "what-if."

¹² Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. Atotech provided information on one proprietary ingredient. W.R. Grace was preparing to transfer information on proprietary chemical ingredients in the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Enthone-OMI, MacDermid, and Shipley) declined to provide proprietary information on their MHC technologies. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients, as available, is presented in this CTSA, but chemical identities, concentrations, and chemical properties are not listed.

¹³ For exposure data from the IPC Workplace Practices Questionnaire, this means that 90 percent of the facilities reported a lower value, and ten percent reported a higher value.

3.4.2 Summary of Human Health Hazards Assessment

Toxicity data in the form of RfDs, RfCs, NOAELs, LOAELs, and cancer slope (cancer potency) factors were compiled for inhalation and dermal pathways. CCs and aquatic toxicity hazard ranks for aquatic species were calculated from aquatic toxicity data on PWB chemicals, but ecological risk characterization was not carried out because the aquatic exposure could not be estimated.

Formaldehyde was the only non-proprietary chemical with an established cancer slope (cancer potency) factor. Other non-proprietary chemicals in the MHC processes are suspected carcinogens, but do not have established slope factors. Dimethylformamide and carbon black have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Dimethylformamide is used by at least one supplier in the electroless copper process. Carbon black is used in the carbon and conductive ink processes. Because slope factors (cancer potency values) are needed for quantitative estimates of cancer risk, cancer risk results are only presented for formaldehyde. Two proprietary chemicals used in the graphite and electroless copper processes, cyclic ether and alkyl oxide, have cancer slope factors. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

3.4.3 Methods Used to Calculate Human Health Risks

Estimates of human health risk from chemical exposure are characterized here in terms of excess lifetime cancer risk, hazard quotient (HQ), and margin of exposure (MOE). This section defines these risk indicators and discusses the methods for calculating each of them.

Cancer Risk

Cancer risks are expressed as the excess probability of an individual developing cancer over a lifetime from chemical exposure. For chemicals classified as carcinogens, an upper bound excess lifetime cancer risk, expressed as a unitless probability, was estimated by the following equation:

cancer risk = LADD x slope factor

where:

Cancer Risk = the excess probability of developing cancer over a lifetime as a result of exposure to a potential carcinogen. The estimated risks are the upper bound excess lifetime cancer risks for an individual. (*Upper bound* refers to the method of determining a slope factor, where the upper bound value for the slope of the dose-response curve is used. *Excess* means the estimated cancer risk is in addition to the already-existing background risk of an individual contracting cancer from all other causes.)

LADD = the lifetime average daily dose, the estimated potential daily dose rate received during the exposure duration, averaged over a 70-year lifetime (in mg/kg-day). LADDs were calculated in the Exposure Assessment (Section 3.2).

Slope factor $(q_1 *)$ is defined in Section 3.3.1.

Non-Cancer Risk Indicators

Non-cancer risk estimates are expressed either as a HQ or as a MOE, depending on whether or not RfDs and RfCs are available. There is generally a higher level of confidence in the HQ than the MOE, especially if the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. If an RfD or RfC is available, the HQ is calculated to estimate risk from chemicals that exhibit chronic, non-cancer toxicity. (RfDs and RfCs are defined in Section 3.3.2.) The HQ is the unitless ratio of the RfD (or RfC) to the potential dose rate. For MHC chemicals that exhibit non-cancer toxicity, the HQ was calculated by:

$$HO = ADD/RfD$$

where:

ADD = average daily dose rate, the amount of a chemical ingested, inhaled, or applied to the skin per unit time, averaged over the exposure duration (in mg/kg-day). ADDs were calculated in the Exposure Assessment (Section 3.2).

The HQ is based on the assumption that there is a level of exposure (i.e., the RfD or RfC) below which it is unlikely, even for sensitive subgroups, to experience adverse health effects. Unlike cancer risk, the HQ does not express *probability* and is not necessarily linear; that is, an HQ of ten does not mean that adverse health effects are ten times more likely to occur than for an HQ of one. However, the ratio of estimated dose to RfD/RfC reflects level of concern.

For chemicals where an RfD or RfC was not available, a MOE was calculated by:

```
MOE = NOAEL/ADD or LOAEL/ADD
```

As with the HQ, the MOE is not a probabilistic statement of risk. The ratio for calculating MOE is the inverse of the HQ, so that a high HQ (exceeding one) indicates a potential concern, whereas a high MOE (exceeding 100 for a NOAEL-based MOE or 1,000 for a LOAEL-based MOE) indicates a low concern level. (NOAELS and LOAELs are defined in Section 3.3.2.) As the MOE increases, the level of concern decreases. (As the HQ increases, the level of concern also increases.)

Both the exposure estimates and toxicity data are specific to the route of exposure (i.e., inhalation, oral, or dermal). Very few RfDs, NOAELs, or LOAELs were available for dermal exposure. If oral data were available, the following adjustments were made to calculate dermal values:

```
\begin{split} RfD_{DER} &= (RfD_{ORAL})(GI~absorption) \\ NOAEL/LOAEL_{DER} &= (NOAEL~or~LOAEL_{ORAL})(GI~absorption) \\ SF_{DER} &= (SF_{ORAL})/GI~absorption) \end{split}
```

where:

RfD_{DER} = reference dose adjusted for dermal exposure (mg/kg-day) NOAEL/LOAEL_{DER} = NOAEL or LOAEL adjusted for dermal exposure (mg/kg-day) SF_{DER} = cancer slope factor adjusted for dermal exposure (mg/kg-day)⁻¹ GI absorption = gastrointestinal absorption efficiency

This adjustment is made to account for the fact that the oral RfDs, NOAELs, and LOAELs are based on an applied dose, while dermal exposure represents an estimated absorbed dose. The oral RfDs, NOAELs, and LOAELs used to assess dermal risks were therefore adjusted using gastro-intestinal (GI) absorption to reflect an absorbed dose. Table 3.35 lists the GI absorption data used in calculating risk from dermal exposure.

Table 3.35 Absorption Percentages

Chemicals ^a GI Tract Absorption (%)		Source of Data		
1,3-Benzenediol	100	NTP, 1992		
2-Ethoxyethanol	100	assumption ^b		
Ammonium Chloride	97	Reynolds, 1982		
Benzotriazole	20	assumption ^b		
Boric Acid	90	EPA, 1990		
Copper (I) Chloride	60	EPA, 1994a		
Diethylene Glycol Ethyl Ether	20	assumption ^b		
Diethylene Glycol Methyl Ether	20	assumption ^b		
Diethylene Glycol n-Butyl Ether	20	assumption ^b		
Dimethylformamide	20	assumption ^b		
Ethanolamine	20	assumption ^b		
Ethylene Glycol	100	ATSDR, 1993		
Fluoroboric Acid	100	Stokinger, 1981		
Formaldehyde	1	EPA, 1995b		
Hydrogen Peroxide	5	default (EPA, 1989)		
Hydroxyacetic Acid	20	assumption ^b		
Isopropyl Alcohol, 2-Propanol	20	assumption ^b		
Methanol	100	Lington & Bevan, 1994		
Palladium	5	Beliles, 1994		
Palladium Chloride	5	Beliles, 1994		
Phenol	20	assumption ^b		
Potassium Cyanide	5	default (EPA, 1989)		
Silver	21	ATSDR, 1990b		
Sodium Chlorite	5	default (EPA, 1989)		
Sodium Cyanide	5	default (EPA, 1989)		
Sodium Sulfate	100	HSDB, 1995		
Stannous Chloride	3	ATSDR, 1992		
Vanillin	6	Kirwin and Galvin, 1993		

^a Includes only those chemicals where dermal HQs or MOEs were calculated. Proprietary chemical data are not presented in order to protect proprietary chemical identities.

^b An assumption of 20 percent was made for organic chemicals when no other data were available.

3.4.4 Results of Calculating Risk Indicators

This section presents the results of calculating risk indicators for both the occupational setting and the ambient (outdoor) environment. When considering these risk characterization results, it should be remembered that the results are intended for use in relative risk comparisons between processes based on a model PWB facility, and should not be used as absolute indicators for potential health risks to MHC line workers or to the public.

Occupational Setting

Estimated cancer risks and non-cancer risk indicators from occupational exposure to MHC chemicals are presented below. It should be noted that no epidemiological studies of health effects among PWB workers were located.

Inhalation Cancer Risk. The electroless copper and graphite processes are the only processes containing chemicals for which a cancer slope (cancer potency) factor is available. Formaldehyde, in the electroless copper process, is the only non-proprietary chemical for which an inhalation cancer risk has been estimated. Formaldehyde has an EPA weight-of-evidence classification of Group B1, a Probable Human Carcinogen. The EPA Group B1 classification is typically based on limited evidence of carcinogenicity in humans, sufficient evidence of carcinogenicity in animals, and additional supporting evidence. The cancer slope factor for formaldehyde is based exclusively on animal data, and is associated with nasal cancer.

Inhalation exposure estimates are based on the assumptions that emissions to indoor air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines. The exposure estimates use 90th percentile modeled air concentrations (0.62 mg/m³ for formaldehyde in the non-conveyorized electroless copper process), which means that, based on the IPC Workplace Practices Questionnaire data and publicly-available information on bath concentrations, approximately 90 percent of the facilities are expected to have lower air concentrations and, therefore, lower risks. Using 90th percentile data is consistent with EPA policy for estimating upper-bound exposures.

With regard to formaldehyde cancer risk, EPA in 1987 issued a risk assessment in which formaldehyde was classified as a Group B1 Probable Human Carcinogen; in addition it was determined to be an irritant to the eyes and respiratory tract. A quantitative risk assessment for cancer was presented using available exposure data and a cancer slope (cancer potency) factor of 0.046 per milligram formaldehyde per kilogram body weight per day. In 1991, EPA proposed a modification of this assessment using additional animal testing and exposure data that had become available. Incorporation of this new data would result in an estimated cancer slope factor of 0.00094 per milligram formaldehyde per kilogram body weight per day, a 50-fold reduction from the current cancer slope factor. However, EPA's Science Advisory Board recommended that formaldehyde cancer risk be presented as a range of risk estimates using data from both the 1987 and 1991 assessments, due to the many uncertainties and data gaps that preclude the use of one assessment to the exclusion of the other. Therefore, upper bound maximum individual cancer risk over a lifetime is presented as a range from 1 x 10⁻³ (one in 1,000) to 2 x 10⁻⁵ (two in 100,000 or one in 50,000) based on a workplace concentration of 0.62 milligrams formaldehyde

per cubic meter of air (over an 8 hour-day) for line operators using the non-conveyorized electroless copper process. It should be pointed out that intensity of exposures to formaldehyde (air concentration) may be more important than average exposure levels over an 8-hour day in increasing cancer risk (Hernandez et al., 1994). The use of modeled, steady state, workplace air concentrations instead of actual monitoring data of average and peak concentrations thus emerges as a significant source of uncertainty in estimating cancer risk to workers exposed to formaldehyde in this industry. The available toxicological data do not indicate that dermal exposure to formaldehyde increases cancer risk, but no dermal cancer studies were located.

To provide further information on the possible variation in occupational formaldehyde exposure and risk estimates, formaldehyde cancer risk is also estimated using average and median values, as would be done for a central tendency exposure estimate.¹⁴ The following median or average parameter values are used:

- The 50th percentile air concentration estimated from the quantitative uncertainty analysis (Section 3.2.3) of 0.055 mg/m³ (compared to the high-end point estimate of 0.62 mg/m³).
- The median job tenure for men in the U.S. of 4.0 years (Bureau of Labor Statistics, 1997) (compared to the 95th percentile of 25 years).
- The average value of 6.8 hrs/day for a line operator from the IPC Workplace Practices Questionnaire (compared to the 90th percentile of 8 hrs/day).
- The average exposure frequency of 250 days/year from the IPC Workplace Practices Questionnaire (compared to the 90th percentile of 306 days/year).

Using these values, there is approximately a 100-fold reduction in estimated exposure with the estimated "central tendency" LADD of $2.6 \times 10^{-4} \text{ mg/kg-day}$. Combined with the slope factor of 0.046 per mg/kg-day, this results in a cancer risk of 1×10^{-5} (one in 100,000). Considering the 50-fold reduction in cancer potency (with a slope factor of 0.00092 per mg/kg-day) the cancer risk would be 2×10^{-9} (one in five million).

Inhalation cancer risk was also estimated for one proprietary chemical, alkyl oxide, in the non-conveyorized electroless copper process. This is discussed to a limited extent, however, to protect proprietary ingredient identity. The line operator inhalation exposure estimate for alkyl oxide¹⁵ results in an estimated upper bound excess individual lifetime cancer risk of 3 x 10⁻⁷ based on high end exposure.

¹⁴ This "central tendency" estimate should also be considered a "what-if" exposure estimate, because of the uncertainty of the process area ventilation rate data.

¹⁵ It should be noted that alkyl oxide is present in the electroless copper and graphite baths at trace concentrations (less than one part per million) and it has a relatively high tendency to evaporate. Based on air modeling estimates, and assuming 100 liter baths, all of this chemical would be released to air within one hour. The assumption that chemical concentration in the baths remains constant over time would result, in this case, in large over-estimates of inhalation exposure. A correction factor was applied to the calculated cancer risks to reflect exposure from the chemical being present for one hour in the baths, at a yearly frequency equal to the bath replacement frequency.

Risks to other workers were assumed to be proportional to the amount of time spent in the process area. Based on the IPC Workplace Practices Questionnaire data, the average line operator spends 1,900 hours per year in the MHC process area. Annual average exposure times (i.e., time spent in the process area) for various worker types from the workplace practices database are listed below. The number in parenthesis is the ratio of average time for that worker type to the average time for a line operator.

- Contract worker: 62 hours per year (0.033).
- Laboratory technician: 1,100 hours per year (0.58).
- Maintenance worker: 930 hours per year (0.49).
- Supervisor: 1,150 hours per year (0.61).
- Wastewater treatment operator: 1,140 hours per year (0.60).
- Other: 1,030 hours per year (0.54).

Dermal Cancer Risk. Dermal cancer risks were estimated for two proprietary chemicals, alkyl oxide and cyclic ether, in the graphite and electroless copper processes. These results are only discussed to a limited extent, however, in order to protect the identity of the proprietary ingredients. Both chemicals have oral cancer slope factors, which were converted for dermal exposure as described in Section 3.4.3. Worker dermal exposure estimates for cyclic ether result in the following estimated upper bound excess individual lifetime cancer risks:

- For conveyorized electroless copper, 8 x 10⁻⁸ for a line operator and 9 x 10⁻⁹ for a laboratory technician.
- For non-conveyorized electroless copper, 4×10^{-7} for a line operator and 9×10^{-9} for a laboratory technician.
- For graphite, 1×10^{-7} for a line operator and 9×10^{-9} for a laboratory technician.

All of these cancer risk estimates are below the concern level of 1 x 10⁻⁶. Worker dermal exposure estimates for alkyl oxide result in the following estimated upper bound excess individual lifetime cancer risks:¹⁶

- For conveyorized electroless copper, 4×10^{-9} for a line operator and 1×10^{-10} for a laboratory technician.
- For non-conveyorized electroless copper, 1×10^{-8} for a line operator and 1×10^{-10} for a laboratory technician.
- For graphite, 8×10^{-8} for a line operator and 6×10^{-9} for a laboratory technician.

Other Potential Cancer Risks. Slope factors (cancer potency values) are needed to calculate estimates of cancer risk. In addition to the chemicals discussed above,

¹⁶ It should be noted that alkyl oxide is present in the electroless copper and graphite baths at trace concentrations (less than one part per million) and it has a relatively high tendency to evaporate. Based on air modeling estimates, and assuming 100 liter baths, all of this chemical would be released to air within one hour. The assumption that chemical concentration in the baths remains constant over time would result in this case, in large over-estimates of dermal exposure. A correction factor was applied to the calculated cancer risks to reflect exposure from the chemical being present for one hour in the baths, at a yearly frequency equal to the bath replacement frequency.

dimethylformamide and carbon black are classified as probable human carcinogens (IARC Group 2B). Like formaldehyde, the evidence for carcinogenic effects is based on animal data. However, unlike formaldehyde, slope factors are not available for either chemical. There are potential cancer risks to workers from both chemicals, but they cannot be quantified. Dimethylformamide is used in the electroless copper process. Workplace exposures have been estimated but cancer potency and cancer risk are unknown. Carbon black is used in the carbon and conductive ink processes. Occupational exposure due to air emissions from the carbon baths is expected to be negligible because the carbon process is typically conveyorized and enclosed. There may be some airborne carbon black, however, from the drying oven steps, which was not quantified in the exposure assessment. Carbon black is also used in one product line of the conductive ink process; exposures from conductive ink were not characterized. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

Non-Cancer Risk. HQs and MOEs for line operators and laboratory technicians from workplace exposures are presented in Appendix E. An HQ exceeding one indicates a potential concern. Unlike cancer risk, HQ does not express probability, only the ratio of the estimated dose to the RfD or RfC, and it is not necessarily linear (an HQ of ten does not mean that adverse health effects are ten times more likely than an HQ of one).

EPA considers high MOE values, such as values greater than 100 for a NOAEL-based MOE or 1,000 for a LOAEL-based MOE, to pose a low level of concern (Barnes and Dourson, 1988). As the MOE decreases, the level of concern increases. Chemicals are noted here to be of potential concern if a NOAEL-based MOE is lower than 1,000, or a MOE based on an effect level that was not specified as a LOAEL is less than 1,000. As with HQ, it is important to remember that the MOE is not a probabilistic statement of risk.

Inhalation risk indicators of concern for non-proprietary chemicals are presented in Table 3.36, and for the known proprietary chemicals in Table 3.37. This includes chemicals of potential concern based on MOE and/or HQ results, as well as cancer risk results for any chemical with a cancer slope factor. Inhalation exposure estimates are based on the assumptions that emissions to air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines.

Dermal risk indicators of concern for non-proprietary chemicals are presented in Table 3.38 and for the known proprietary chemicals in Table 3.39. This includes chemicals of potential concern based on MOE and/or HQ results, as well as cancer risk results for any chemical with a cancer slope factor. Dermal exposure estimates are based on the assumption that both hands are routinely immersed in the bath and that the worker does not wear gloves.

It should be noted that Tables 3.36 through 3.39 do not include chemicals for which toxicity data were unavailable.

Table 3.36 Summary of Human Health Risk Results From Inhalation Exposure for Selected Non-Proprietary Chemicals

Chemical of	·	Risk Indicator ^{a, b}		Potential Health Effects
Concerna	Electroless Copper, non-conveyorized	Non-Formaldehyde Electroless Copper, non-conveyorized	Tin-Palladium, non-conveyorized	
Copper (I) Chloride	MOE ^c (1) 420, line operator LOAEL	NA	NA	Long-term exposure to copper dust can irritate nose, mouth and eyes, and cause dizziness. Long-term exposure to high levels of copper may cause liver damage. Copper is not known to cause cancer. The seriousness of the effects of copper can be expected to increase with both level and length of exposure.
Ethanolamine	MOE (3) 68, line operator LOAEL	NA	MOE (2,3) 34, line operator LOAEL	Ethanolamine is a strong irritant. Animal studies showed that the chemical is an irritant to respiratory tract, eyes, and skin. No data were located for inhalation exposure in humans.
2-Ethoxyethanol	HQ ^c (4) 140, line operator	NA	NA	In animal studies 2-ethoxyethanol caused harmful blood effects including destruction of red blood cells and resulting in the release of hemoglobin (hemolysis) and male reproductive effects at high exposure levels. The seriousness of the effects can be expected to increase with both level and length of exposure. No data were located for inhalation exposure in humans.
Ethylene Glycol	MOE (3,5) 500, line operator Human Exposure Data	NA	NA	In humans, low levels of vapors produce throat and upper respiratory irritation. When ethylene glycol breaks down in the body, it forms chemicals that crystallize and that can collect in the body and prevent kidneys from working. The seriousness of the effects can be expected to increase with both level and length of exposure.

3.4 RISK CHARACTERIZATION

Chemical of		Risk Indicator ^{a, b}		Potential Health Effects
Concerna	Electroless Copper, non-conveyorized	Non-Formaldehyde Electroless Copper, non-conveyorized	Tin-Palladium, non-conveyorized	
Formaldehyde	cancer risk 2 x 10 ⁻⁵ to 1 x 10 ⁻³ , line operator ^d MOE 0.48, line operator LOAEL	NA	NA	Formaldehyde in animals produces nasal cancer (from inhalation) at low levels. In humans, exposure at low levels in air produces skin irritation and throat and upper respiratory irritation. The seriousness of these effects can be expected to increase with both level and length of exposure.
Formic Acid	MOE 90, line operator NOAEL	NA	NA	Formic acid is a strong irritant to the skin, eyes, and mucous membranes based on clinical evidence in humans and animal toxicity data. There is also clinical evidence to indicate adverse effects on kidney function in humans, as well as central nervous system effects, such as visual and mental disturbances, following repeated exposures to high concentrations of formic acid.
Methanol	MOE (1,4,6) 370, line operator Human Exposure Data	NA	NA	Long-term exposure to methanol vapors can cause headache, irritated eyes and dizziness at high levels. No harmful effects were seen when monkeys were exposed to highly concentrated vapors of methanol. When methanol breaks down in the tissues, it forms chemicals that can collect in the tissues or blood and lead to changes in the interior of the eye causing blindness.
Sodium Hydroxide	MOE 910, line operator LOAEL	NA	NA	Sodium hydroxide is corrosive by all routes of exposure, with numerous case reports of poisonings in humans. Contact with the skin begins to cause immediate damage but not immediate pain. Acute and repeated exposures both result in damage due to the corrosive properties of the chemical. Carcinomas of the esophagus, larynx, and trachea have been reported in humans several, years after ingestion of high concentrations of sodium hydroxide.

Chemical of		Risk Indicator ^{a, b}		Potential Health Effects
Concerna	Electroless Copper, non-conveyorized	= = '		
Sulfuric Acid		24, line operator	30, line operator NOAEL	Sulfuric acid is a very strong acid and can cause structural damage to skin and eyes. Humans exposed to sulfuric acid mist at low levels in air experience a choking sensation and irritation of lower respiratory passages.

^a This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

^b How to read this table:

<u>A</u>	(B)
C, D	
E	

- A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk)
- B: Process bath(s) in which the chemical is used. Numbers in parenthesis indicate the process bath(s) in which the chemical is used:
 - (1) electroless copper bath
- (2) accelerator bath
- (3) cleaner/conditioner bath
- (4) anti-tarnish bath

(5) microetch bath

- (6) catalyst bath
- (7) predip bath

(8) acid dip bath

- C: Value calculated for risk indicator (cancer risk, HQ, or MOE).
- D: Type of worker for which risk results are presented (line operator or laboratory technician).
- E: Type of toxicity data used for MOE: NOAEL, LOAEL or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

NA: Not Applicable.

^c There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD.

^d To provide further information on the possible variation of formaldehyde exposure and risk, an additional exposure estimate is provided using average and median values (rather than high-end) as would be done for a central tendency exposure estimate. This results in approximately a 35-fold reduction in occupational formaldehyde exposure and risk.

Table 3.37 Summary of Human Health Risk Results from Inhalation Exposure for Selected Proprietary Chemicals

Code Name for Chemical of	Risk Indicator	Potential Health Effects	
Concern	Electroless Copper, non- conveyorized		
Alkyl Oxide	cancer risk 3 x 10 ⁻⁷ , line operator	Probable human carcinogen.	
Alkene Diol		Exposure to low levels may result in irritation of the throat and upper respiratory tract.	

Note: Baths not specified to protect proprietary chemical identities.

A C, D E

- A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk)
- C: Value calculated for risk indicator (cancer risk, HQ, or MOE).
- D: Type of worker for which risk results are presented (line operator or laboratory technician).
- E: Type of toxicity data used for MOE: NOAEL, LOAEL or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

For inhalation exposure, 2-ethoxyethanol is the only MHC chemical with an HQ greater than one; this is for a line operator in the non-conveyorized electroless copper process. Chemicals with MOEs below the above-mentioned levels for inhalation exposure include the following:

- For non-conveyorized electroless copper: copper (I) chloride, ethanolamine, ethylene glycol, formaldehyde, formic acid, methanol, sodium hydroxide, sulfuric acid, and one proprietary chemical for a line operator.
- For non-conveyorized tin-palladium: ethanolamine and sulfuric acid for a line operator.
- For non-conveyorized non-formaldehyde electroless copper: sulfuric acid for a line operator.

Dermal risk indicators of concern for non-proprietary chemicals are presented in Table 3.38 and for the known proprietary chemicals in Table 3.39. Dermal exposure estimates are based on the assumption that workers do not wear gloves and that all non-conveyorized lines are operated by manual hoist. Chemicals with HQs from dermal exposure greater than one include:

- Formaldehyde for a line operator in the non-conveyorized electroless copper and conveyorized electroless copper processes.
- Stannous chloride for a line operator in the non-conveyorized electroless copper, non-formaldehyde electroless copper (non-conveyorized), non-conveyorized tin-palladium, and conveyorized tin-palladium processes.
- One proprietary chemical for a line operator in the conveyorized electroless copper process.

^a This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

^b How to read this table:

^c There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD.

Table 3.38 Summary of Human Health Risk Results From Dermal Exposure for Selected Non-Proprietary Chemicals

Chemical of		Tunium Treutim Tush	Risk Indicator ^{a, b}		•	Potential Health Effects
Concerna	Electroless Copper, non-conveyorized	Electroless Copper, conveyorized	Non-Formaldehyde Electroless Copper, non-conveyorized	Tin-Palladium, non-conveyorized	Tin-Palladium, conveyorized	
Copper (I) Chloride	MOE ° (1) 0.96, line operator 39, laboratory tech. LOAEL	MOE 4.3, line operator 39, laboratory tech. LOAEL	NA	MOE 1.9, line operator 190, laboratory tech. LOAEL	5.2, line operator	No data were located for health effects from dermal exposure in humans.
Fluoroboric Acid	2.0, line operator	8.5, line operator 80, laboratory tech.	NA	4.6, line operator 460, laboratory tech.	MOE (2) 13, line operator 460, laboratory tech. Human Exposure Data	In humans, fluoroboric acid produces strong caustic effects leading to structural damage to skin and eyes.
Formaldehyde	HQ (1) 15, line operator LOAEL	HQ (1) 3.4, line operator LOAEL	NA	NA	NA	In humans, exposure at low levels in air produces skin irritation. The seriousness of these effects can be expected to increase with both level and length of exposure.
Palladium	MOE 20, line operator 820, laboratory tech. LOAEL	MOE (6) 92, line operator 820, laboratory tech. LOAEL	NA	MOE 5.6, line operator 560, laboratory tech. LOAEL	MOE (6) 20, line operator 560, laboratory tech. LOAEL	No specific information was located for health effects from dermal exposure in humans.
Palladium Chloride	NA	NA	NA	MOE (6) 8.9 line operator 890, laboratory tech. LOAEL	MOE (6) 32, line operator 890, laboratory tech. LOAEL	Long-term dermal exposure in humans produces contact dermatitis.
Sodium Chlorite	MOE (2) 17, line operator NOAEL	MOE (2) 73, line operator NOAEL	MOE (2) 15, line operator NOAEL	NA	NA	No specific information was located for health effects from dermal exposure to sodium chlorite in humans. Animal studies showed that the chemical produces moderate irritation of skin and eyes.

Chemical of		Risk Indicator ^{a, b}				
Concerna	Electroless Copper, non-conveyorized	Electroless Copper, conveyorized	Non-Formaldehyde Electroless Copper, non-conveyorized	Tin-Palladium, non-conveyorized	Tin-Palladium, conveyorized	
Stannous		NA	` ` '			Mild irritation of the skin
Chloride	3.6, line operator		3.7, line operator	15, line operator	' I	and mucous membrane has
						been shown from inorganic
						tin salts. However, no
						specific information was
						located for dermal exposure
						to stannous chloride in
						humans. Stannous chloride
						is only expected to be
						harmful at high doses; it is
						poorly absorbed and leaves
						the body rapidly.

^a This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

^b How to read this table:



- A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk).
- B: Process bath(s) in which the chemical is used. Numbers in parenthesis indicate the process bath(s) in which the chemical is used:
 - (1) electroless copper bath
- (2) accelerator bath

- (3) cleaner/conditioner bath
- (4) anti-tarnish bath

(5) microetch bath

(6) catalyst bath

(7) predip bath

(8) acid dip bath

- C: Value calculated for risk indicator (cancer risk, HQ, or MOE).
- D: Type of worker for which risk results are presented (line operator or laboratory technician).
- E: Type of toxicity data used for MOE: NOAEL; LOAEL; or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

NA: Not Applicable.

^c There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD.

Table 3.39 Summary of Human Health Risk Results from Dermal Exposure for Selected Proprietary Chemicals

Code Name			Risk Indicator ^a			Potential Health Effects
for Chemical of Concern	Electroless Copper, non-conveyorized	Electroless Copper, conveyorized	Graphite, conveyorized	Organic-Palladium, non-conveyorized	Organic-Palladium, conveyorized	
Nitrogen Heterocycle		MOE 510, line operator	NA	NA	NA	No data were located for health effects from dermal exposure in humans.
Palladium Salt	NA	NA	NA	MOE 1.5, line operator 450, lab. tech.	MOE 8.0, line operator 450, lab. tech.	Exposure may result in skin irritation and sensitivity.
	MOE 71, line operator	MOE 320, line operator	NA	NA	NA	No data were located for health effects from dermal exposure in humans.
	4 x 10 ⁻⁷ , line operator	8 x 10 ⁻⁸ , line operator		NA	NA	Possible/probable human carcinogen.
Alkyl Oxide	1 x 10 ⁻⁸ , line operator	4 x 10 ⁻⁹ , line operator		NA	NA	Long-term dermal exposure in humans produces contact dermatitis; probable human carcinogen.
Tin Salt	NA	HQ 1.1, line operator	NA	NA	NA	No data were located for health effects from dermal exposure in humans. Inorganic tin compounds may irritate the eyes, nose, throat, and skin.

^a MOE based on LOAEL.

Note: Baths not specified to protect proprietary chemical identities.

A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk). Α $\overline{C,D}$ C: Value calculated for risk indicator (cancer risk, HQ, or MOE). Ε

D: Type of worker for which risk results are presented (line operator or laboratory technician).

E: Type of toxicity data used for MOE: NOAEL; LOAEL; or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

b This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

^c How to read this table:

d There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD. NA: Not Applicable.

Chemicals with NOAEL-based MOEs lower than 100, or LOAEL-based MOEs or other MOEs lower than 1,000 for dermal exposure include the following:

- For non-conveyorized electroless copper: copper (I) chloride, fluoroboric acid, palladium, sodium chlorite, and two proprietary chemicals for a line operator; copper (I) chloride, fluoroboric acid, and palladium for a laboratory technician.
- For conveyorized electroless copper: copper (I) chloride, fluoroboric acid, palladium, sodium chlorite, and two proprietary chemicals for a line operator; copper (I) chloride, fluoroboric acid, and palladium for a laboratory technician.
- For non-conveyorized non-formaldehyde electroless copper: sodium chlorite for a line operator.
- For non-conveyorized tin-palladium: copper (I) chloride, fluoroboric acid, palladium and palladium chloride for a line operator and laboratory technician.
- For conveyorized tin-palladium: copper (I) chloride, fluoroboric acid, palladium and palladium chloride for a line operator and laboratory technician.
- For non-conveyorized organic-palladium: one proprietary chemical for a line operator and laboratory technician.
- For conveyorized organic-palladium: one proprietary chemical for a line operator and laboratory technician.

Ambient (Outdoor) Environment

Cancer Risk. As with the occupational setting, the electroless copper and graphite processes are the only processes for which a cancer risk to humans in the ambient (outdoor) environment has been estimated. Formaldehyde is the only non-proprietary chemical with cancer risks estimated for the general population. These results are for both conveyorized and non-conveyorized electroless copper processes, assuming that emissions from both process configurations are vented to the outside. The upper bound excess¹⁷ individual lifetime cancer risk for nearby residents from the non-conveyorized electroless copper process from formaldehyde inhalation was estimated to range from 2×10^{-9} to 1×10^{-7} . The risk for nearby residents from the conveyorized electroless copper process was estimated to range from 6×10^{-9} to 3×10^{-7} . Again, the higher values (3×10^{-7} for conveyorized and 1×10^{-7} for non-conveyorized) are based on a LADDs of 7.0×10^{-6} mg/kg-day and 2.6×10^{-6} mg/kg-day, respectively, and a slope (cancer potency) factor of 0.046 per mg/kg-day. The lower values (6×10^{-9} for conveyorized and 2×10^{-9} for non-conveyorized) take into account a possible 50-fold reduction in inhalation unit risk.

The discussion of reduction in estimated cancer risk from Section 3.4.1 applies to these results as well. Formaldehyde has been classified as Group B1, a Probable Human Carcinogen based on limited evidence of carcinogenicity in humans, sufficient evidence of carcinogenicity in animals, and additional supportive evidence. These estimates indicate low concern and are

¹⁷ *Upper bound* refers to the method of determining a slope factor, where the upper bound value (generated from a certain probability statement) for the slope of the dose-response curve is used. *Excess* means the estimated cancer risk is in addition to the already-existing background risk of an individual contracting cancer from all other causes.

interpreted to mean that, over a lifetime, an individual resident is expected to have no more than one excess chance in ten million of developing cancer from exposure to formaldehyde from a nearby facility using the non-conveyorized electroless copper process, or one excess chance in three million of developing cancer from exposure to formaldehyde from the conveyorized electroless copper risk is slightly higher due to the larger surface areas of conveyorized baths, resulting in higher modeled air emission rates.

The graphite and electroless copper processes contain one known proprietary chemical, alkyl oxide, with an inhalation cancer slope factor. Inhalation exposure to cyclic ether, the other proprietary chemical with a cancer slope factor, is assumed negligible because the chemical is non-volatile and is not used in an air-sparged bath. The upper bound excess individual lifetime cancer risk for nearby residents from the (conveyorized) graphite process from inhalation of alkyl oxide was estimated to be 9 x 10⁻¹¹. This estimate indicates low concern and is interpreted to mean that, over a lifetime, an individual resident is expected to have no more than one excess chance in 11 billion of developing cancer from exposure to alkyl oxide from a conveyorized graphite process. The upper bound excess individual lifetime cancer risk for nearby residents from the electroless copper process from inhalation of alkyl oxide was estimated to be 1 x 10⁻¹¹ for the non-conveyorized process and 3 x 10⁻¹¹ for the conveyorized electroless copper process. These estimates also indicate low concern and are interpreted to mean that, over a lifetime, an individual resident is expected to have no more than one excess chance of developing cancer in 100 billion for non-conveyorized electroless copper, and no more than one excess chance in 33 billion for conveyorized electroless copper from inhalation exposure to alkyl oxide.

None of the other process alternatives use chemicals for which cancer slope factors were available, so no other cancer risks were estimated. Other identified chemicals in the MHC processes are suspected carcinogens, but do not have established slope factors. Dimethylformamide and carbon black have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Dimethylformamide is used in the electroless copper process. Carbon black is used in the carbon and conductive ink processes. Carbon black is not expected to be released to outside air in any significant amount from a facility using the carbon process. This is because carbon black is not a volatile compound, and aerosol releases are not expected because it is not used in an air-sparged bath. Conductive ink exposures and risks were not characterized. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

Non-Cancer Risk. Appendix E presents HQs for estimated chemical releases to ambient air, and subsequent inhalation by residents near a model facility. Chemicals below the emission rate cutoff of 23 kg/year are not included because below this emission rate exposures are

¹⁸ It should be noted that alkyl oxide is present in the electroless copper and graphite baths at trace concentrations (less than one part per million) and it has a relatively high tendency to evaporate. Based on air modeling estimates, and assuming 100 liter baths, all of this chemical would be released to air within one hour. The assumption that chemical concentration in the baths remains constant over time would result, in this case, in large over-estimates of inhalation exposure. A correction factor was applied to the calculated cancer risks to reflect exposure from the chemical being present for one hour in the baths, at a yearly frequency equal to the bath replacement frequency.

expected to be negligible. All HQs are less than one for ambient exposure to the general population, indicating low concern.

These results suggest there is low risk to nearby residents, based on incomplete but best available data. Data limitations include the use of modeled air concentrations using average data rather than site-specific, measured concentrations. For estimating ambient (outdoor) air concentrations, one key assumption is that no air pollution control technologies are used to remove airborne chemicals from facility air prior to venting it to the outside. Other data limitations are the lack of waterborne and solid waste data to characterize exposure routes in addition to inhalation, and lack of toxicity data for many chemicals.

Appendix E presents MOEs from ambient air exposures. The chemicals included are those above the emission rate cutoff and for which NOAEL or LOAEL data were available. (Also if an HQ could be calculated an MOE was not.) All MOEs for ambient exposure are greater than 1,000 for all processes, indicating low concern from the estimated air concentrations.

3.4.5 Uncertainties

An important component of any risk characterization is the identification and discussion of uncertainties. There are uncertainties involved in the measurement and selection of hazard data, and in the data, models and scenarios used in the Exposure Assessment. Any use of the risk characterization should include consideration of these uncertainties.

Uncertainties in the Exposure Assessment include the following:

- Accuracy of the description of exposure setting: how well the model facility used in the
 assessment characterizes an actual facility; the likelihood of exposure pathways actually
 occurring (scenario uncertainty).
- Missing data and limitations of workplace practices data: this includes possible effects of any chemicals that may not have been included (e.g., minor ingredients in the formulations, proprietary chemical identities not disclosed by suppliers); possible effects of side reactions in the baths which were not considered; and questionnaire data with limited facility responses.
- Estimating exposure levels from averaged data and modeling in the absence of measured, site-specific data.
- Data limitations in the Source Release Assessment: releases to surface water and land could not be characterized quantitatively.
- Chemical fate and transport model applicability and assumptions: how well the models and assumptions represent the situation being assessed and the extent to which the models have been validated or verified (model uncertainty).
- Parameter value uncertainty, including measurement error, sampling (or survey) error, parameter variability, and professional judgement.

Key assumptions made in the Exposure Assessment are discussed in Section 3.4.1.

Uncertainties in the hazard data (typically encountered in a hazard assessment) include the following:

- Using dose-response data from high dose studies to predict effects that may occur at low levels.
- Using data from short-term studies to predict the effects of long-term exposures.
- Using dose-response data from laboratory animals to predict effects in humans.
- Using data from homogeneous populations of laboratory animals or healthy human populations to predict the effects on the general human population, with a wide range of sensitivities. (This uncertainty is due to natural variations in human populations.)
- Using LOAELs and NOAELs in the absence of peer-reviewed RfDs and RfCs.
- Possible increased or decreased toxicity resulting from chemical interactions.
- Assuming a linear dose-response relationship for cancer risk (in this case for formaldehyde).
- Effects of chemical mixtures not included in toxicity testing (effects may be independent, additive, synergistic, or antagonistic).
- Possible effects of substances not evaluated because of a lack of chronic/subchronic toxicity data.

Another source of uncertainty comes from use of structure-activity relationships (SARs) for estimating human health hazards in the absence of experimental toxicity data. Specifically, this was done for: dimethylaminoborane, EDTA (sodium salt), fluoroboric acid, graphite, magnesium carbonate, m-nitrobenzene sulfonic acid, monopotassium peroxymonosulfate, palladium chloride, phosphoric acid, potassium bisulfate, potassium carbonate, potassium persulfate, potassium sulfate, p-toluene sulfonic acid, sodium bisulfate, sodium hypophosphite, and sodium persulfate. SARs were also used for ten proprietary chemicals.

Uncertainties in assessing risk from dermal exposure come from the use of toxicological potency factors from studies with a different route of exposure than the one under evaluation (i.e., using oral toxicity measures to estimate dermal risk). This was done for nine chemicals with oral RfDs, 15 chemicals with oral NOAELs (as noted in Tables 3.25 and 3.26), and two proprietary chemicals with oral cancer slope factors. Uncertainties in dermal risk estimates also stem from the use of default values for missing gastrointestinal absorption data. Specifically, this was done for benzotriazole, diethylene glycol ethyl ether, diethylene glycol n-butyl ether, ethanolamine, 2-ethoxyethanol, hydrogen peroxide, hydroxyacetic acid, isopropyl alcohol, potassium cyanide, sodium chlorite, and sodium cyanide.

Finally, the risk characterization does not address the potential adverse health effects associated with acute exposure to peak levels of chemicals. This type of exposure is especially important when evaluating developmental risks associated with exposure.

3.4.6 Conclusions

This risk characterization uses a health-hazard based framework and a model facility approach to compare the health risks of one MHC process technology to the risks associated which switching to an alternative technology. As much as possible, reasonable and consistent assumptions are used across alternatives. Data to characterize the model facility and exposure patterns for each process alternative were aggregated from a number of sources, including PWB shops in the U.S. and abroad, supplier data, and input from PWB manufacturers at project

meetings. Thus, the model facility is not entirely representative of any one facility, and actual risk could vary substantially, depending on site-specific operating conditions and other factors.

When using the results of this risk characterization to compare health effects among alternatives, it is important to remember that this is a screening level rather than a comprehensive risk characterization, both because of the predefined scope of the assessment and because of exposure and hazard data limitations. It should also be noted that this approach does not result in any absolute estimates or measurements of risk, and even for comparative purposes, there are several important uncertainties associated with this assessment.

Primary among these uncertainties is the incomplete identification of all chemicals among the process alternatives because of trade secret considerations. This factor alone precludes any definitive recommendations among the processes because the health risks from all relevant chemicals could not be evaluated. It should be noted here also that chemical suppliers to the PWB industry are in the sole position to fill these data gaps for a more complete assessment. Without that, conclusions can only be drawn based on the best available information. It should also be noted that chemical suppliers are required to report on an MSDS (under 29 CFR Part 1910.1200) that a product contains hazardous chemicals, if present at one percent or greater of a product composition, or 0.1 percent or greater for carcinogens. The chemical manufacturer may withhold the specific chemical identity from the MSDS, provided that the MSDS discloses the properties and effects of the hazardous chemical. A review of the available MSDSs indicates that there are hazardous chemicals listed as trade secret ingredients: three in electroless copper, one in graphite, three in organic-palladium, and one in tin-palladium. Section 2.1.4 presents these results and discusses the use of MSDS information further.

Another significant source of uncertainty is the limited data available for dermal toxicity and the use of oral to dermal extrapolation when dermal toxicity data were unavailable. There is high uncertainty in using oral data for dermal exposure and in estimating dermal absorption rates, which could result in either over- or under-estimates of exposure and risk.

A third significant source of uncertainty is from the use of structure-activity relationships to estimate toxicity in the absence of measured toxicity data, and the lack of peer-reviewed toxicity data for many MHC chemicals. Other uncertainties associated with the toxicity data include the possible effects of chemical interactions on health risks, and extrapolation of animal data to estimate human health risks from exposure to formaldehyde and other PWB chemicals.

¹⁹ Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. Atotech provided information on one proprietary ingredient. W.R. Grace was preparing to transfer information on proprietary chemical ingredients in the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Enthone-OMI, MacDermid, and Shipley) declined to provide proprietary information on their MHC technologies. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients, as available, is presented in this CTSA, but chemical identities, concentrations, and chemical properties are not listed.

Another major source of uncertainty in estimating exposure is the reliance on modeled data (i.e., modeled air concentrations) to estimate worker exposure. It should also be noted that there is no comparative evaluation of the severity of effects for which HQs and MOEs are reported.

The Exposure Assessment for this risk characterization used, whenever possible, a combination of central tendency and high-end assumptions, as would be used for an overall high-end exposure estimate. Some values used in the exposure calculations, however, are better characterized as "what-if," especially pertaining to bath concentrations, use of gloves, and process area ventilation rates for a model facility. Because some part of the exposure assessment for both inhalation and dermal exposures qualifies as a "what-if" descriptor, the entire assessment should be considered "what-if."

Among those health risks evaluated, it can be concluded that alternatives to the non-conveyorized electroless copper process appear to present a lower overall risk, due to reduced cancer risk to PWB workers when the use of formaldehyde is eliminated. Other adverse effects from chronic, low level exposures to chemicals in the alternative processes provide some basis for additional comparison. While alternatives to electroless copper appear to pose less overall risk, there is insufficient information to compare these alternatives among themselves to determine which of the alternatives pose the least risk.

Occupational Exposures and Risks

Health risk to workers are estimated for inhalation exposure to vapors and aerosols from MHC baths and for dermal exposure to MHC bath chemicals. Inhalation exposure estimates are based on the assumptions that emissions to indoor air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines. Dermal exposure estimates are based on the assumption that workers do not wear gloves and that all non-conveyorized lines are operated by manual hoist. Dermal exposure to line operators on non-conveyorized lines is estimated for routine line operation and maintenance (e.g., bath replacement, filter replacement, etc.), and on conveyorized lines for bath maintenance activities alone.

Risk results indicate that alternatives to the non-conveyorized electroless copper process pose lower occupational risks. However, in addition to several chemicals in the non-conveyorized electroless copper process, there are occupational inhalation risk concerns for some chemicals in the non-formaldehyde electroless copper and tin-palladium non-conveyorized processes as well. There are also occupational risk concerns for dermal contact with some chemicals in the electroless copper, organic-palladium, and tin-palladium processes for either conveyorized or non-conveyorized equipment.

Cancer Risk. The non-conveyorized electroless copper process contains the only non-proprietary chemical for which an occupational cancer risk has been estimated (for formaldehyde). Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. The upper bound excess individual cancer risk estimate for line operators in the non-conveyorized electroless copper process from formaldehyde inhalation may be as high as

one in a thousand, but may be 50 times less, or one in 50,000.²⁰ Risks to other workers were assumed to be proportional to the amount of time spent in the process area, which ranged from three to 61 percent of the risk for a line operator.

Inhalation cancer risk was also estimated for one proprietary chemical, alkyl oxide, in the non-conveyorized electroless copper process. The line operator inhalation exposure estimate for alkyl oxide results in an estimated upper bound excess individual life time cancer risk of 3×10^{-7} (one in three million) based on high end exposure. Cancer risks less than 1×10^{-6} (one in one million) are generally considered to be of low concern.

Additionally, dermal cancer risks were estimated for two proprietary chemicals, cyclic ether and alkyl oxide, in the graphite and electroless copper processes. For the conveyorized graphite process, the dermal cancer risks for a line operator may be as high as 8×10^{-8} (about one in ten million) for the alkyl oxide and 1×10^{-7} (one in ten million) for the cyclic ether. The upper bound cancer risks for a laboratory technician were much less than the risks for a line operator. The cancer risks for a laboratory technician were 6×10^{-9} (one in 200 million) for alkyl oxide and 9×10^{-9} (one in 100 million) for cyclic ether.

For non-conveyorized electroless copper, the dermal cancer risks for the line operator may be as high as 4×10^{-7} (one in two million) for cyclic ether and 1×10^{-8} (one in 100 million) for alkyl oxide. The estimated upper bound cancer risks for a laboratory technician were much less than the cancer risk for a line operator. The estimated cancer risks for a laboratory technician were 9×10^{-9} (one in 100 million) for cyclic ether and 1×10^{-10} (one in ten billion) for alkyl oxide.

For conveyorized electroless copper, the dermal cancer risk for a line operator may be as high as 8×10^{-8} (about one in ten million) for cyclic ether and 4×10^{-9} (one in 200 million) for alkyl oxide. The estimated upper bound cancer risks for a laboratory technician were much less than the cancer risks for a line operator. The estimated cancer risks for a laboratory technician were 9×10^{-9} (one in 100 million) for cyclic ether and 1×10^{-10} (one in ten billion) for alkyl oxide.

Other identified chemicals in the MHC processes are suspected carcinogens. Dimethylformamide and carbon black have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Also, a proprietary trisodium acetate amine has been classified as a possible human carcinogen. Dimethylformamide and the proprietary chemical are used in the electroless copper process and carbon black is used in the carbon and conductive ink processes. There are potential cancer risks to workers from these chemicals, but because there are no slope factors, the risks cannot be quantified.

To provide further information on the possible variation of formaldehyde exposure and risk, an additional exposure estimate is provided using average and median values (rather than high-end) as would be done for a central tendency exposure estimate. This results in approximately a 100-fold reduction in occupational formaldehyde exposure and risk.

Non-Cancer Risk. For non-cancer risk, HQs greater than one were estimated for occupational exposures to chemicals in the non-conveyorized and conveyorized electroless copper processes, the non-conveyorized and conveyorized tin-palladium processes, and the non-conveyorized non-formaldehyde electroless process. Also, several chemicals had estimated MOEs lower than 100 or LOAEL-based MOEs lower than 1,000 for occupational exposures in the non-conveyorized and conveyorized electroless copper processes, non-conveyorized and conveyorized organic-palladium processes, and non-conveyorized non-formaldehyde electroless copper process.

Based on calculated occupational exposure levels, there may be adverse health effects to workers exposed to these chemicals with a HQ exceeding 1.0 or an MOE less than 100 or 1,000. However, it should be emphasized that these conclusions are based on screening level estimates.

These numbers are used here for relative risk comparisons between processes, and should not be used as absolute indicators for potential health risks to MHC line workers.

Ambient (Outdoor) Exposures and Risks

Public health risk was estimated for inhalation exposure for the general populace living near a facility. Public exposure estimates are based on the assumption that emissions from both conveyorized and non-conveyorized process configurations are vented to the outside. The risk indicators for ambient exposures to humans, although limited to airborne releases, indicate low concern for nearby residents. The upper bound excess individual cancer risk for nearby residents from formaldehyde in the non-conveyorized electroless copper process was estimated to be from approaching zero to 1 x 10⁻⁷ (one in ten million) and from approaching zero to 3 x 10⁻⁷ (one in three million) for the conveyorized electroless copper process. Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. The upper bound excess individual cancer risk for nearby residents from the proprietary alkyl oxide in the conveyorized graphite process was estimated to be from approaching zero to 9 x 10⁻¹¹ (one in 11 billion); in the nonconveyorized electroless copper process from approaching zero to 1 x 10⁻¹¹ (one in 100 billion). and in the conveyorized electroless copper process from approaching zero to 3 x 10⁻¹¹ (one in 33 billion). All hazard quotients are less than one for ambient exposure to the general population, and all MOEs for ambient exposure are greater than 1,000 for all processes, indicating low concern from the estimated air concentrations for chronic non-cancer effects.

Ecological Hazards

The CTSA methodology typically evaluates ecological risk in terms of risks to aquatic organisms in streams that receive treated or untreated effluent from manufacturing processes. Stream concentrations were not available, however, and could not be estimated because of data limitations (i.e., insufficient characterization of constituents and their concentrations in facility wastewater). The upper limit of the aquatic release (and thus, its consequent exposure/risk) is controlled by regulation; the degree of control varies by site. Section 4.3, Regulatory Status, discusses the pertinent regulations. Because exposure (i.e., stream concentrations) could not be quantified, ecological (aquatic) risk is not characterized. Instead, an ecological hazard assessment was performed (Section 3.3.3), based only on chemical toxicity to aquatic organisms. The results of this evaluation are summarized briefly here.

3.4 RISK CHARACTERIZATION

Concern concentrations were estimated for MHC chemicals using an established EPA method. A CC is an acute or chronic toxicity value divided by an assessment factor (AsF). AsFs are dependent on the amount and type of toxicity data contained in a toxicity profile and reflect the amount of uncertainty about the potential effects associated with a toxicity value. CCs were determined for aquatic species (e.g., *Daphnia*, algae, and/or fish). The lowest CC is for copper sulfate, based on fish toxicity data.

Chemicals are also ranked for aquatic toxicity concern levels using established EPA criteria (high, moderate, and low concern) based on the available toxicity data. The number of chemicals with a high aquatic hazard concern level include nine in the electroless copper process, two in carbon, two in conductive ink, none in conductive polymer, three in graphite, three in nonformaldehyde electroless copper, two in organic-palladium, and nine in the tin-palladium process.

3.5 PROCESS SAFETY ASSESSMENT

Process safety is the concern of employers and employees alike. Each company has the obligation to provide its employees with a safe and healthy work environment, while each employee is responsible for his/her own safe personal work habits. An effective process safety program identifies potential workplace hazards and, if possible, seeks to eliminate or at least reduce their potential for harm. In the MHC process of PWB manufacturing, these hazards may be either chemical hazards or process hazards. Chemicals used in the MHC process can be hazardous to worker health and therefore must be handled and stored properly, using appropriate personal protective equipment and safe operating practices. Automated equipment can be hazardous to employees if safe procedures for cleaning, maintaining, and operating are not established and regularly performed. These hazards can result in serious injury and health problems to employees, and potential damage to equipment.

The U.S. Department of Labor and the Occupational Safety and Health Administration (OSHA) have established safety standards and regulations to assist employers in creating a safe working environment and protect workers from potential workplace hazards. In addition, individual states may also have safety standards regulating chemical and physical workplace hazards for many industries. Federal safety standards and regulations affecting the PWB industry can be found in the Code of Federal Regulation (CFR) Title 29, Part 1910 and are available by contacting your local OSHA field office. State and local regulations are available from the appropriate state office. This section of the CTSA presents chemical and process safety concerns associated with the MHC baseline and substitutes, as well as OSHA requirements to mitigate these concerns.

3.5.1 Chemical Safety Concerns

As part of its mission, OSHA's Hazard Communication Standard (29 CFR 1910.1200) requires that chemical containers be labeled properly with chemical name and warning information [.1200(f)], that employees be trained in chemical handling and safety procedures [.1200(h)], and that a MSDS be created and made available to employees for every chemical or formulation used in the workplace [.1200(g)]. Each MSDS must be in English and include information regarding the specific chemical identity of the hazardous chemical(s) involved and the common names. In addition, information must be provided on the physical and chemical characteristics of the hazardous chemical; known acute and chronic health effects and related health information; exposure limits; whether the chemical is a carcinogen; emergency and first-aid procedures; and the identification of the organization preparing the data sheet. Copies of MSDSs for all of the chemicals used must be kept and made available to workers who may come into contact with the process chemicals during their regular work shift.

In order to evaluate the chemical safety concerns of the various MHC processes, MSDSs for 172 chemical products comprising eight MHC technology categories were collected and reviewed for potential hazards to worker safety. The results of that review are summarized and discussed in the categories below. General information on OSHA storage and handling requirements for chemicals in these hazard categories are located in the process safety section of this chapter. For a more detailed description of OSHA storage and handling requirements for

MHC chemical products in these categories contact your area OSHA field office or state technical assistance program for assistance.

Flammable, Combustible, and Explosive MHC Chemical Products

A breakdown of MHC chemical products that when in concentrated form are flammable, combustible, explosive, or pose a fire hazard is presented in Table 3.40. The following lists OSHA definitions for chemicals in these categories, and discusses the data presented in the table.

Table 3.40 Flammable, Combustible, Explosive, and Fire Hazard Possibilities for MHC Processes

MHC Process	Bath Type		Hazardous	Property ^a	
		Flammable	Combustible	Explosive	Fire Hazard
Carbon	Cleaner	2 (2)			
	Conditioner	3 (3)			
	Other (Anti-Tarnish)	2 (2)			
Conductive Ink	Print Ink			5 (5)	
Conductive Polymer ^b	Polymer	1 (3)			
Electroless Copper	Accelerator	1 (5)			
	Anti-Tarnish	2 (4)			
	Cleaner/Conditioner	1 (8)		1 (8)	
	Electroless Copper	2 (25)	1 (25)		1 (25)
	Microetch	1 (9)			
Graphite	Microetch				1 (4)
Non-Formaldehyde	Accelerator	1 (2)			
Electroless Copper	Anti-Tarnish	1(1)			
	Microetch	1 (4)			
Palladium	Accelerator			1 (10)	1 (10)
	Cleaner/Conditioner	1 (6)	1 (6)		
	Other (Anti-Tarnish)	1 (3)			

^a Table entries are made in the following format - # of products meeting OSHA definition for the given hazardous property as reported in the products MSDSs (Total # of products in the process bath). A **blank** entry means that none of the products for the specific process bath meet the OSHA reporting criteria for the given property. Example: For the palladium process accelerator bath, 1 (10) means that one of the ten products in the bath were classified as explosive per OSHA criteria as reported on the products MSDSs.

Flammable - A flammable chemical is defined by OSHA [29 CFR 1910.1200(c)] as one of the following:

• An aerosol that, when tested by the method described in 16 CFR 1500.45, yields a flame projection exceeding 18 inches at full valve opening, or a flashback at any degree of valve opening.

^b Hazardous properties based on German equivalent of MSDS, which may not have same reporting requirements of U.S. MSDS.

- A gas that has: 1) at ambient temperature and pressure, forms a flammable mixture with air at a concentration of 13 percent by volume or less; or 2) when it, at ambient temperature and pressure, forms a range of flammable mixtures with air wider than 12 percent by volume, regardless of the lower limit.
- A liquid that has a flashpoint below 100 °F (37.8 °C), except any mixture having components with flashpoints of 100 °F (37.8 °C) or higher, the total of which make up 99 percent or more of the total volume of the mixture.
- A solid, other than a blasting agent or explosive as defined in 29 CFR 1910.109(a), that is liable to cause fire through friction, absorption of moisture, spontaneous chemical change, or retained heat from manufacturing or processing, or which can be ignited readily and when ignited burns so vigorously and persistently as to create a serious hazard.

Twenty chemical products are reported as flammable according to MSDS data. While all of the products have flashpoints near or below 100 °F, several of the products reported as flammable have flashpoints greater than 200 °F with one as high as 400 °F. Although several chemical products are flammable in their concentrated form, most chemical baths in the MHC process line contain non-flammable aqueous solutions.

Combustible Liquid - As defined by OSHA [29 CFR 1910.1200(c)], a liquid that is considered combustible has a flashpoint at or above 100 °F (37.8 °C), but below 200 °F (93.3 °C), except any mixture having components with flashpoints of 200 °F (93.3 °C), or higher, the total volume of which make up 99 percent or more of the total volume of the mixture. Two chemical products have been reported as combustible by their MSDSs, both with flashpoints above 155 °F.

Explosive - As defined by OSHA [29 CFR 1910.1200(c)], a chemical is considered explosive if it causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature. Seven chemical products are reported as explosive by their MSDSs.

Fire Hazard - A chemical product that is a potential fire hazard is required by OSHA to be reported on the product's MSDS. According to MSDS data, three chemical products are reported as potential fire hazards.

3.5.2 Corrosive, Oxidizer, and Reactive MHC Chemical Products

A breakdown of MHC chemical baths containing chemical products that are corrosive, oxidizers, or reactive in their concentrated form is presented in Table 3.41. The table also lists process baths that contain chemical products that may cause a sudden release of pressure when opened. The following lists OSHA definitions for chemicals in these categories and discusses the data presented in the table.

Table 3.41 Corrosive, Oxidizer, Reactive, Unstable, and Sudden Release of Pressure Possibilities for MHC Processes

MHC Process	Bath Type		На	zardous F	Property ^a	
		Corrosive	Oxidizer	Reactive	Unstable	Sudden Release of Pressure
Carbon	Cleaner Conditioner Microetch	2 (2) 3 (3)	2 (2)	2 (2)		
Conductive Polymer ^b	Catalyst Conductive Polymer Microetch	2 (3) 2 (3) 1 (1)				
Electroless Copper	Accelerator Catalyst Cleaner/Conditioner Electroless Copper Microetch Predip	1 (5) 5 (10) 5 (8) 11 (25) 3 (9) 4 (6)	1 (5) 5 (9)	3 (5) 2 (10) 2 (8) 5 (25) 2 (9) 2 (6)	1 (9)	1 (9)
Graphite	Fixer Graphite Microetch	1 (1) 1 (3) 2 (4)	1 (4)		1 (4)	
Non-Formaldehyde Electroless Copper	Accelerator Electroless Copper Microetch	2 (6) 2 (4)	1 (2) 2 (4)	1 (2) 1 (6) 2 (4)		1 (4)
Palladium	Accelerator Catalyst Cleaner/Conditioner Microetch Other Predip	4 (10) 4 (9) 1 (6) 2 (3) 1 (4)		1 (10) 1 (9) 1 (5)	1 (5)	

^a Table entries are made in the following format - # of products meeting OSHA definition for the given hazardous property as reported in the product's MSDSs (Total # of products in the process bath). A **blank** entry means that none of the products for the specific process bath meet the OSHA reporting criteria for the given property. Example: For the graphite process microetch bath, 2 (4) means that two of the four products in the bath were classified as corrosive per OSHA criteria as reported by the products MSDSs.

Corrosive - As defined by OSHA (29 CFR 1910.1200 [Appendix A]), a chemical is considered corrosive if it causes visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact, as determined by the test method described by the U.S. Department of Transportation 49 CFR Part 173 Appendix A. This term does not apply to chemical action on inanimate surfaces. A review of MSDS data found that 59 MHC chemical products are reported as corrosive in their concentrated form. Some MHC baths may also be corrosive, but MSDSs do not provide data for the process chemical baths once they are prepared.

^b Hazardous properties based on German equivalent of MSDS, which may not have same reporting requirements of U.S. MSDS.

Oxidizer - As defined by OSHA (29 CFR 1910.1200[c]), an oxidizer is a chemical other than a blasting agent or explosive as defined by OSHA [29 CFR 1910.109(a)], that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases. Twelve chemical products are reported as oxidizers according to MSDS data.

Reactive - A chemical is considered reactive if it is readily susceptible to change and the possible release of energy. EPA gives a more precise definition of reactivity for solid wastes. As defined by EPA (40 CFR 261.23), a solid waste is considered reactive if it exhibits any of the following properties: 1) is normally unstable and readily undergoes violent change without detonating; 2) reacts violently or forms potentially explosive mixtures with water; 3) when mixed with water, generates toxic gases, vapors, or fumes in a quantity that can present a danger to human health or the environment (for a cyanide or sulfide bearing waste, this includes exposure to a pH between 2 and 12.5); 4) is capable of detonation or explosive reaction if subjected to a strong initiated source or if heated under confinement; or 5) is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure. A review of MSDS data found that 25 chemical products from four different MHC processes are considered reactive.

Unstable - As defined by OSHA (29 CFR 1910.1200[c]), a chemical is unstable if in the pure state, or as produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shock, pressure, or temperature. Only three chemical products are reported as unstable according to MSDS data.

Sudden Release of Pressure - OSHA requires the reporting of chemical products that, while stored in a container subjected to sudden shock or high temperature, causes a pressure increase within the container that is released upon opening. MSDS data indicated only two chemical products that are potential sudden release of pressure hazards.

3.5.3 MHC Chemical Product Health Hazards

A breakdown of MHC process baths that contain chemical products that are sensitizers, acute or chronic health hazards, or irreversible eye damage hazards in their concentrated form is presented in Table 3.42. Also discussed in this section are MHC chemical products that are potential eye or dermal irritants and suspected carcinogens. The following presents OSHA definitions for chemicals in these categories and discusses the data in Table 3.42 where appropriate.

Table 3.42 Sensitizer, Acute and Chronic Health Hazards, and Irreversible Eye Damage Possibilities for MHC Processes

MHC Process	Bath Type		Hazard	ous Property ^a	
		Sensitizer	Acute Health Hazard	Chronic Health Hazard	Irreversible Eye Damage
Carbon	Carbon Black Cleaner Conditioner Microetch Other (Anti-Tarnish)		3 (4) 1 (2) 3 (3) 2 (2) 2 (2)	3 (4) 1 (2) 3 (3) 2 (2)	4 (4) 2 (2) 2 (3) 2 (2) 2 (2)
Conductive Ink	Print Ink				2 (5)
Conductive Polymer ^b	Catalyst Conductive Polymer Microetch				3 (3) 2 (3) 1 (1)
Electroless Copper	Accelerator Anti-Tarnish Catalyst Cleaner/Conditioner Electroless Copper Microetch Predip		1 (5) 2 (4) 2 (10) 1 (8) 5 (25) 3 (9)	2 (4) 2 (10) 1 (8) 4 (25) 1 (9)	1 (5) 2 (4) 6 (10) 3 (8) 13 (25) 4 (9) 5 (6)
Graphite	Cleaner/Conditioner Fixer Graphite Microetch		3 (4) 2 (3) 3 (4)	2 (4)	1 (1) 1 (3) 2 (4)
Non-Formaldehyde Electroless Copper	Accelerator Catalyst Electroless Copper Microetch		1 (2) 2 (2) 3 (6) 3 (4)	2 (2) 2 (6) 1 (4)	4 (6) 3 (4)
Organic-Palladium ^b	Conductor Microetch Postdip				2 (2) 1 (1) 1 (1)
Tin-Palladium	Accelerator Catalyst Cleaner/Conditioner Microetch Other Acid Dip	2 (6)	1 (10) 3 (9) 1 (6) 2 (5) 2 (3)	3 (9) 2 (5)	9 (10) 4 (9) 2 (6) 3 (5) 3 (3) 1 (1)

^a Table entries are made in the following format - # of products meeting OSHA definition for the given hazardous property as reported in the product's MSDSs (Total # of products in the process bath). A **blank** entry means that none of the products for the specific process bath meet the OSHA reporting criteria for the given property. Example: For the palladium process cleaner/conditioner bath, 2 (6) means that two of the six products in the bath were classified as sensitizers per OSHA criteria as reported by the products MSDSs.

^b Hazardous properties based on German equivalent of MSDS, which may not have same reporting requirements of U.S. MSDS.

Sensitizer - A sensitizer is defined by OSHA [29 CFR 1910.1200 Appendix A (mandatory)] as a chemical that causes a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to the chemical. Only two chemical products were reported as sensitizers by MSDS data, both palladium MHC process chemicals.

Acute and Chronic Health Hazards - As defined by OSHA (29 CFR 1910.1200 Appendix A), a chemical is considered a health hazard if there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. Health hazards are classified using the criteria below:

- Acute health hazards are those whose effects occur rapidly as a result of short-term exposures, and are usually of short duration.
- Chronic health hazards are those whose effects occur as a result of long-term exposure, and are of long duration.

Chemicals that are considered a health hazard include carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, nuerotoxins, agents which act on the hematopoietic system, and agents which damage the lungs, skin, eyes, or mucous membranes.

A review of MSDS data found 51 chemical products reported as potentially posing acute health hazards, and 33 chemical products potentially posing chronic health hazards. OSHA does not require reporting of environmental hazards such as aquatic toxicity data, nor are toxicity data on MSDSs as comprehensive as the toxicity data collected for the CTSA. OSHA health hazard data are presented here for reference purposes only, and are not used in the risk characterization component of the CTSA.

Carcinogen - As defined by OSHA (29 CFR 1910.1200 Appendix A), a chemical is considered to be a carcinogen if: 1) it has been evaluated by the International Agency for Research on Cancer (IARC), and found to be a carcinogen or potential carcinogen; 2) it is listed as a carcinogen or potential carcinogen in the Annual Report on Carcinogens published by the National Toxicology Program (NTP); or 3) it is regulated by OSHA as a carcinogen. Formaldehyde, which is used as a reducing agent in the electroless copper process, is a suspected human carcinogen. A review of MSDS data found that six chemical products were reported as potential carcinogens. All of the products contain formaldehyde and are utilized in the electroless copper bath of the traditional electroless copper process.

Dermal or Eye Irritant - An irritant is defined by OSHA [29 CFR 1910.1200 Appendix A (mandatory)] as a chemical, which is not corrosive, but which causes a reversible inflammatory effect on living tissue by chemical action at the site of contact. A chemical is considered a dermal or eye irritant if it is so determined under the testing procedures detailed in 16 CFR 1500.41- 42. A review of MSDS data found that all but six of the 181 MHC chemical products reviewed are reported as either dermal or eye irritants.

Irreversible Eye Damage - Chemical products that, upon coming in contact with eye tissue, can cause irreversible damage to the eye are required by OSHA to be identified as such on the product's MSDS. A review of MSDS data found that 91 chemical products are reported as having the potential to cause irreversible eye damage.

3.5.4 Other Chemical Hazards

MHC chemical products that have the potential to form hazardous decomposition products are presented below. In addition, chemical product incompatibilities with other chemicals or materials are described, and other chemical hazard categories presented. The following lists OSHA definitions for chemicals in these categories and summarizes the MSDS data where appropriate.

Hazardous Decomposition - A chemical product, under specific conditions, may decompose to form chemicals that are considered hazardous. With few exceptions, the MSDS data for the chemical products in the MHC process indicate the possibility of decomposition to form a potentially hazardous chemical. Each chemical product should be examined to determine its decomposition products so that potentially dangerous reactions and exposures can be avoided. The following are examples of hazardous decomposition of chemical products that are employed in the MHC alternatives:

- When heated, a chemical product used to create an electroless copper bath can generate toxic formaldehyde vapors.
- If allowed to heat to dryness, a graphite bath process chemical could result in gas releases of ammonia, carbon monoxide, and carbon dioxide.
- Thermal decomposition under fire conditions of certain chemical bath constituents of a palladium cleaner/conditioner bath can result in releases of toxic oxide gases of nitrogen and carbon.

Incompatibilities - Chemical products are often incompatible with other chemicals or materials with which they may come into contact. A review of MSDS data found that all of the MHC processes have chemical products with incompatibilities that can pose a threat to worker safety if the proper care is not taken to prevent such occurrences. Incompatibilities reported range from specific chemicals or chemical products, such as acids or cyanides, to other materials, such as rubber or textiles, like wood and leather. Chemical incompatibilities that are common to products from all the MHC processes include acids, alkalis, oxidizers, metals, and reducing agents. Incompatibilities were also found to exist between chemical products used on the same process line. Individual chemical products for each process bath should be closely examined to determine specific incompatibilities and care should be taken to avoid contact with incompatible chemicals and chemical products, textiles, and storage containers.

The following are examples of chemical incompatibilities that exist for chemical products that are employed in the MHC alternatives:

• An electroless copper bath contains chemical products that, when contacted with hydrochloric acid which is present in other electroless copper process baths, will result in reaction forming bis-chloromethyl ether, an OSHA-regulated carcinogen.

- Violent reactions can result when a chemical product of the conductive polymer catalyst bath comes into contact with concentrated acids or reducing agents, both of which are used in PWB manufacturing processes.
- A microetch bath of a graphite process contains chemicals that will react to form hazardous gases when contacted with other chemical products containing cyanides, sulfides, or carbides.
- Hazardous polymerization of a particular conductive ink product can occur when the
 product is mixed with chemicals products containing amines, anhydrides, mercaptans, or
 imidazoles.

Other Chemical Hazard Categories - OSHA requires the reporting of several other hazard categories on the MSDSs for chemicals or chemical products that have not already been discussed above. These additional categories include chemical products that are:

- Water-reactive (react with water to release a gas that presents a health hazard).
- Pyrophoric (will ignite spontaneously in air at temperatures below 130 °F).
- Stored as a compressed gas.
- Classified as an organic peroxide.
- Chemicals that have the potential for hazardous polymerization.

A review of MSDS data indicated that none of the chemical products are reported as being water-reactive, pyrophoric, a compressed gas, an organic peroxide, or as having the potential for hazardous polymerization.

3.5.5 Process Safety Concerns

Exposure to chemicals is just one of the safety issues that PWB manufacturers may have to deal with during their daily activities. Preventing worker injuries should be a primary concern for employers and employees alike. Work-related injuries may result from faulty equipment, improper use of equipment, bypassing equipment safety features, failure to use personal protective equipment, and physical stresses that may appear gradually as a result of repetitive motions (i.e., ergonomic stresses). Any or all of these types of injuries may occur if proper safeguards or practices are not in place and adhered to. An effective worker safety program includes:

- An employee training program.
- Employee use of personal protective equipment.
- Proper chemical storage and handling.
- Safe equipment operating procedures.

The implementation of an effective worker safety program can have a substantial impact on business, not only in terms of direct worker safety, but also in reduced operating costs as a result of fewer days of absenteeism, reduced accidents and injuries, and lower insurance costs. Maintaining a safe and efficient workplace requires that both employers and employees recognize and understand the importance of worker safety and dedicate themselves to making it happen.

Employee Training

A critical element of workplace safety is a well-educated workforce. To help achieve this goal, the OSHA Hazard Communication Standard requires that all employees at PWB manufacturing facilities (regardless of the size of the facility) be trained in the use of hazardous chemicals to which they are exposed. A training program should be instituted for workers, especially those operating the MHC process, who may come into contact with, or be exposed to, potentially hazardous chemicals. Training may be conducted by either facility staff or outside parties who are familiar with the PWB manufacturing process and the pertinent safety concerns. The training should be held for each new employee, as well as periodic retraining sessions when necessary (e.g., when a new MHC process is instituted), or on a regular schedule. The training program should explain to the workers the types of chemicals with which they work and the precautions to be used when handling or storing them; when and how personal protection equipment should be worn; and how to operate and maintain equipment properly.

Storing and Using Chemicals Properly

Because the MHC process requires handling of a variety of chemicals, it is important that workers know and follow the correct procedures for the use and storage of the chemicals. Much of the use, disposal, and storage information about MHC process chemicals may be obtained from the MSDSs provided by the manufacturer or supplier of each chemical or formulation. Safe chemical storage and handling involves keeping chemicals in their proper place, protected from adverse environmental conditions, as well as from other chemicals with which they may react. Examples of supplier recommended storage procedures found on the MSDSs for MHC chemicals are listed below:

- Store chemical containers in a cool, dry place away from direct sunlight and other sources of heat.
- Chemical products should only be stored in their properly sealed original containers and labeled with the generic name of the chemical contents.
- Incompatible chemical products should never be stored together.
- Store flammable liquids separately in a segregated area away from potential ignition sources or in a flammable liquid storage cabinet.

Some products have special storage requirements and precautions listed on their MSDSs (e.g., relieving the internal pressure of the container periodically). Each chemical product should be stored in a manner consistent with the recommendation on the MSDS. In addition, chemical storage facilities must be designed to meet any local, state, and federal requirements that may apply.

Not only must chemicals be stored correctly, but they must also be handled and transported in a manner which protects worker safety. Examples of chemical handling recommendations from suppliers include:

- Wear appropriate protective equipment when handling chemicals.
- While transporting chemicals, do not use open containers.
- Use only spark-proof tools when handling flammable chemicals.

• Transfer chemicals using only approved manual or electrical pumps to prevent spills created from lifting and pouring.

Proper chemical handling procedures should be a part of the training program given to every worker. Workers should also be trained in chemical spill containment procedures and emergency medical treatment procedures in case of chemical exposure to a worker.

Use of Personal Protective Equipment

OSHA has developed several personal protective equipment standards that are applicable to the PWB manufacturing industry. These standards address general safety and certification requirements (29 CFR Part 1910.132), the use of eye and face protection (Part 1910.133), head protection (Part 1910.135), foot protection (Part 1910.136), and hand protection (Part 1910.138). The standards for eye, face, and hand protection are particularly important for the workers operating the MHC process where there is close contact with a variety of chemicals, of which nearly all irritate or otherwise harm the skin and eyes. In order to prevent or minimize exposure to such chemicals, workers should be trained in the proper use of personal safety equipment.

The recommended personal protective equipment for a worker handling chemicals is also indicated on the MSDS. For the majority of MHC chemicals, the appropriate protective equipment indicated by the MSDS includes:

- Goggles to prevent the splashing of chemical into the eyes.
- Chemical aprons or other impervious clothing to prevent splashing of chemicals on clothing.
- Gloves to prevent dermal exposure while operating the process.
- Boots to protect against chemical spills.

Other items less widely suggested include chemically resistant coveralls and hats. In addition to the personal protective equipment listed above, some MSDSs recommended that other safety equipment be readily available. This equipment includes first aid kits, oxygen supplies (SCBA), and fire extinguishers.

Other personal safety considerations are the responsibility of the worker. Workers should be discouraged from eating or keeping food near the MHC process. Because automated processes contain moving parts, workers should also be prohibited from wearing jewelry or loose clothing, such as ties, that may become caught in the machinery and cause injury to the worker or the machinery itself. In particular, the wearing of rings or necklaces may lead to injury. Workers with long hair that may also be caught in the machinery should be required to securely pull their hair back or wear a hair net.

Use of Equipment Safeguards

In addition to the use of proper personal protection equipment for all workers, OSHA has developed safety standards (29 CFR Part 1910.212) that apply to the actual equipment used in a PWB MHC process. Among the safeguards recommended by OSHA that may be used for conveyorized equipment are barrier guards, two-hand trip devices, and electrical safety devices.

Safeguards for the normal operation of conveyor equipment are included in the standards for mechanical power-transmission apparatus (29 CFR Part 1910.219) and include belts, gears, chains, sprockets, and shafts. PWB manufacturers should be familiar with the safety requirements included in these standards and should contact their local OSHA office or state technical assistance program for assistance in determining how to comply with them.

In addition to normal equipment operation standards, OSHA also has a lockout/tagout standard (29 CFR Part 1910.147). This standard is designed to prevent the accidental start-up of electric machinery during cleaning or maintenance operations that apply to the cleaning of conveyorized equipment as well as other operations. OSHA has granted an exemption for minor servicing of machinery provided the equipment has other appropriate safeguards, such as a stop/safe/ready button which overrides all other controls and is under the exclusive control of the worker performing the servicing. Such minor servicing of conveyorized equipment can include clearing fluid heads, removing jammed panels, lubricating, removing rollers, minor cleaning, adjusting operations, and adding chemicals. Rigid finger guards should also extend across the rolls, above and below the area to be cleaned. Proper training of workers is required under the standard whether lockout/tagout is employed or not. For further information on the applicability of the OSHA lockout/tagout standard to MHC process operations, contact the local OSHA field office.

Occupational Noise Exposure

OSHA has also developed standards (29 CFR Part 1910.95) that apply to occupational noise exposure. These standards require protection against the effects of noise exposure when the sound levels exceed certain levels specified in the standard. No data was collected on actual noise levels from MHC process lines, but one PWB manufacturer suggested protective measures may be needed to reduce noise levels from air knife ovens on carbon and graphite lines. This manufacturer installed baffles on his system to reduce noise levels (Kerr, 1997).

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